MWTS Testing—E.N.R. Test Cell Baseline Calibration & Phase 2 Activities at Cypress Wetland

Prepared for

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1.0 Executive Summary for Fifth Quarter of Operational Testing

1.1 Summary of Results

This report provides the status and results for the fifth quarter of operational testing at the ENR for the MWTS project, as of December 31, 2000. With the close of the third quarter the baseline calibration period was completed and the fourth quarter was the first full quarter of experimental operation. Water quality sampling for field and laboratory parameters has followed the schedule defined in the MWTS research plan and work plan. In this quarter chemical treatment evaluations continued at the ENR. The baseline calibration period at the Seminole Reservation site began in July 2000.

This section is a synopsis of results described in subsequent sections. The reader is encouraged to refer to the subsequent sections for specific numeric details of the trends summarized here.

The subsequent sections of the report cover the following topics:

Section 2—Background and Purpose
Section 3—Meteorological Data for ENR
Section 4—ENR Water Quality Sampling
Section 5—Phase II Operations at the Seminole Reservation
Section 6—Marsh Readiness and Ionic Conditioning

1.1.1 Everglades Nutrient Removal Test Cell Experimental Results

Introduction

Testing of chemical treatment followed by marsh conditioning was initiated at the Everglades Nutrient Removal Project (ENR) in three cells of the North Test Cell (NTC) site and at two cells in the South Test Cell site

- ➢ North Test Cells
  - ▪ NTC 2   iron (Fe) treatment cell
  - ▪ NTC 3   control cell
  - ▪ NTC 4   aluminum (Al) treatment
- ➢ South Test Cells
  - ▪ STC 6   control cell
  - ▪ STC 7   aluminum (Fe) treatment cell

Hydrologic Regime

The target operating depth for the Test Cells is 0.33 m and the target hydraulic loading rate (HLR) is 10 centimeters per day. For the quarter water depth in the test cells has ranged from 0. 3 to 0.5 m. HLRs were in the range of 8 to 10 cm/d.

Water Balance

A water balance for each test cell was calculated from the measured and estimated inflows, and changes in storage volume. Because the test cells are lined seepage loss is assumed to be zero. Outflow has been calculated by difference since the second quarter of testing due to the uncertainty in estimating outflow from the weir settings. At the conclusion of the baseline period (Q1 and Q2) a water balance for each test cell was developed (see 2nd Quarterly Report). In that analysis inflow and outflow balanced for only one of the six test cells, NTC 3. The high positive and negative residuals for the other five test cells indicated variation in one or more outflows and storage in response to a variety of factors. Over the course of the baseline period, water balance residuals were expected to become relatively small. The project team implemented a quality control plan for field data collection. Some of the steps include the following: 1) less frequent adjustment of weir height in water level 2) careful measurement of weir height setting, and 3) verify that our measurement of flow over the weirs is accurate. In addition we assessed the value of calculating the water balance on a daily basis rather than on a monthly average. The water balance calculations for Q1 and Q2 indicated that the magnitude of the residuals remained high.

Water Quality

This section provides a very brief synopsis of treatment effects at the ENR test cells for the quarter; in-depth discussion is provided in Section 4 of the report.

All chemical treatments pilot units (two in the NTC and one in the STC) operated through the entire quarter. Results, comparing constituent concentration of the raw inflow with test cell outflow, from the northern and southern ENR sites are as follows:

- Fe and Al treatments reduced TP, TPP, SRP, TDP, DOP, TN, TKN, org-N, and TOC concentrations relative to the control. Color was reduced in both Al treatments.

- It appears that the wetland contributed TDP over the period of pilot plant operation (control cell results) but overall the treatment cells demonstrated net TP removal (NTC 2 and NTC 4), or little net change (STC 7).

- TPP in the pilot unit effluent was removed in the wetland.

These trends are generally consistent with those observed in the previous quarter (Q4).

Phosphorus

In the fifth quarter control cell NTC3 raw water inflow TP concentration was greater than that from the wetland outflow. This trend was often reversed at the STCs for treatment (STC7) and control cell (STC6). For both locations inflow TP was relatively evenly split between particulate and dissolved fractions.

Raw water influent [TP] was in a range of 90 to 230 ppb at the NTCs and 30 to 180 ppb at the STCs. These ranges are very similar to the previous quarter (Q4) and represent an increase over previous quarters for both sites. NTC treatment wetland outflow TP concentrations were lower for the treatments compared to the control. Iron treatment resulted in a 50-70% reduction and aluminum a 50-85% reduction. The [TP] and [TPP] concentrations fall from inflow to outflow. This result indicates that particulate P from the respective chemical

treatment effluent was removed at the head of the wetland. The treatment effect on wetland outflow is evident in the time series (Appendix B) and wetland water quality gradient plots (Appendix C).

At the southern ENR location outflow [TP] was 10% to 20% lower for the aluminum treatment versus control cell STC6.

Phosphorus Species

Chemical analyses provide a breakdown of TP into total particulate P (TPP), total dissolved P(TDP), dissolved organic P(DOP) and soluble reactive P(SRP). A summary of each P-species is as follows:

- TPP—raw water influent TPP levels at NTCs were typically greater than or equal to levels at STCs (Appendix B). Water quality gradient data (Appendix C) show treatment effect on wetland outflow [TPP] for the fifth quarter. Outflow TP concentration was higher for the control (NTC3) relative to the chemical treatments (NTC2 and NTC4). As noted above, for the treatment period, [TP] and[TPP] drop across the wetland for both chemical treatment cells at the north site. For the quarter the northern treatment cells had inflow [TPP] in the range of 60 to 80 ppb. Monthly average outflow TPP concentration was 20 to 39 ppb for the iron treatment and the control, but averaged 12 ppb for the aluminum treatment. For the STCs, inflow [TPP] averaged 30ppb. The outflow concentration for the control cell was equal to or higher than the inflow; in contrast, the outflow concentration for the aluminum treatment averaged 20 ppb.

- TDP—NTC control cell (NTC 3) and treatments (NTC2 and NTC4) had lower outflow TDP concentrations as compared to inflow values. The average outflow [TDP] (= 15 ppb) for the two treatments (Fe and Al) were lower than the control outflow concentrations, which averaged 30 ppb. The effect of treatment is apparent at the NTCs with significant reductions in [TDP] compared to the control (Appendix B). For the STCs the monthly wetland influent [TDP] average ranged from 14 to 56 ppb and the wetland effluent ranged from 15 to 56 ppb. For the STCs there was no clear chemical treatment effect for this parameter.

- SRP—Influent [SRP] rose steadily at the northern site for the quarter from approximately 18 ppb at the start to 115 ppb at the close. Influent [SRP] was higher at NTCs compared to STCs (averages of 45 ppb versus 11 ppb). At the southern site outflow [SRP] is typically less than 10 ppb for all three test cells. Outflows from the NTCs (treatments and control) averaged less than 10 ppb. [SRP].

Nitrogen

The average Q5 raw water inflow [TN] was slightly lower for STCs as compared to NTCs (3.05 mg/l for NTC and 2.71 mg/L for STC). At both locations the inflow and outflow TN values are approximately equal for the control cells (NTC3, STC6). NTC and STC results show a treatment effect with lower wetland effluent [TN] for the treatments as compared to the controls. At the NTCs the aluminum treatment reduces nitrogen to a greater extent than the iron.

Other Water Quality Parameters

For several of the remaining parameters the inflow and outflow concentrations are approximately equal at the respective test cells. Included in this group are TSS, magnesium, and aluminum. Other observations for water quality trends in Q5 include:

- Sulfate—NTC treatments (both Fe, Al) slightly reduced outflow sulfate concentrations compared to the control, NTC3. Comparison of STC6 and STC7 were less clear.

- Color—Chemical treatments at both the northern and southern sites reduced color relative to the control. At the north site, the Al treatment resulted in lower color values than the Fe treatment. The control treatments at both sites had little apparent effect on color.

- TOC—Results for the fifth quarter are similar to those for color, the chemical treatments at both locations resulted in lower outflow [TOC], compared to the controls. At the north site the Al treatment resulted in lower TOC values relative to the iron treatment.

- Dissolved silica—Results follow the pattern noted for color and TOC, reduced concentration for outflow as compared to inflow for Al and Fe treatments.

- Fe, Cl—The ferric chloride treatment (NTC2) resulted in higher outflow concentrations of iron and chloride than the either the control or the aluminum treatment. At the remaining test cells the inflow and outflow values are approximately equal for iron and chloride.

- Hardness—Average NTC outflow hardness tended to be slightly lower than the average inflow value. The trend was most pronounced in the Fe treatment (NTC2). No trend was discernable in the STCs.

- Alkalinity. —The alkalinity inflow/outflow relationship varied by sample date in all cells except STC7 (Al treatment) where outflow alkalinity was distinctly lower than that of the inflow.

Mass Balance

Phosphorus

The general P removal trends observed over the treatment period at the ENR test cells continued in Q5. At the northern site iron, control and aluminum treatments removed 80%, 56% and 83% of influent P load, respectively. Month to month results were quite variable for the STCs, but in keeping with results from previous quarters there was a net export of P with average removal rates -35% in the control cell and -10% in the Al treatment cell.

Phosphorus Species

A summary of each P-species is as follows:

- **TPP**—patterns of removals for TPP are similar to those of TP at both locations. The NTCs show regular pattern of net removals on monthly and cumulative basis. The average TPP removal rate for the quarter was approximately 55% for the control, 80% for the iron treatment, and 85% for the aluminum treatment. The STCs exhibited

month to month variation between positive and negative removal rates for control and treatment, consistent with results from the previous quarter.

- **TDP**—All NTCs showed net TDP removal for the quarter, with the rates for treatment cells much higher than the control cell percent removal. Net removal rates for the iron and aluminum treatment cells averaged 72% and 82%, respectively, versus 65% for the control. The STC control and treatment cell removal rates varied between positive and negative as in the previous the quarter. On a cumulative basis, however, the aluminum treatment (STC7) had a net positive removal rate, while the control (STC6) had a net negative rate.

- **SRP**—The northern test cells sowed net removal for SRP over the quarter with removal rates of 77% for control and 90% for the two treatments. For the STCs SRP removal rates were variable month to month for both the treatment and control, but the net cumulative removal rate remained positive for both.

- **DOP**—The month to month DOP removal rates are variable at NTC3, the control, but are moderate to high (40-90%) for the iron and aluminum treatments. These results are consistent with those observed for the previous quarter. For the STCs removal rates were variable on a monthly basis, but negative on a cumulative basis for the control and slightly positive for aluminum.

Nitrogen

A treatment effect is apparent at the NTCs for the fifth quarter and the previous quarters. TN removal averaged 37% for the iron treatment, 60% for the aluminum treatment, and 10% for the control cell. At the south site, the quarterly mean percent mass removal rate was 13% for aluminum but negative for the control.

1.1.2 Chemical Treatment Pilot Plant Operation

The operational anomalies from the previous quarter carried over into the fifth quarter. During Q4 it appeared that the chemical treatment systems at both sites were not reducing phosphorus to the target levels predicted by all previous jar-testing. A focused investigation of pilot plant operation was carried in out early May. Based on that investigation adjustments were made to plant operations. By early July it was clear that even with the operational adjustments made in May and June, the pilot plants were still not producing the low levels of TDP that were expected, even at extremely high coagulant doses. Some of the laboratory data were questioned at this time. In September a laboratory switch from PPB Labs to DB Labs was made for phosphorus analyses (TP, TDP, TPP, SRP, and DOP); since the time of the laboratory switch, many of the chemical plant effluent TDP samples are now being reported at less than 10 ppb. Despite dramatic reductions in effluent TSS from the plants since recirculation was stopped in early September, effluent TP results are typically in the 30 to 50 ppb range at the North plants, and around 20 ppb at the South plant. This may be an artifact of ongoing carryover of phosphorus bound in metal hydroxide floc from the sludge storage tanks , rather than an indication of the TP leaving the plate settlers under current operational conditions.

By the close of the quarter the chemical plants were operating as expected from earlier jar testing, with TDP concentrations typically less than 10 ppb. It is probable that this has been

the case throughout most of the study; erroneous lab data hid the actual results, and prevented the investigators from seeing the effect of operational changes over time.

TP concentrations are higher than the desired target of 10 ppb from the chemical plants: An evaluation of the TP concentration leaving the plate settlers is underway.

1.1.3 Phase II Operations at the Seminole Reservation

The Cypress demonstration project is located on the Seminole Indian Reservation. It was separated into two parts. Part 1 included construction of hydraulic system components and a period of hydration and conditioning of the 4-acre wetlands demonstration area. The work completed included construction of the raw water pump and associated electrical work, transmission piping to the wetlands demonstration area, and a splash pad at the discharge point. Part 2 was to include construction of a chemical treatment system and a treatment pond and subsequent operation of the combined wetland and chemical treatment system. Wetland hydration began in late July 2000 and was scheduled to continue through December 2000. The Phase 2 project was halted in October 1, 2000, however, at the request of the Seminole Tribe.

1.1.4 Evaluation of Marsh Readiness

Marsh readiness refers to the ensemble water quality characteristics of the water leaving the treatment wetland and the similarity of that water to appropriate receiving waters. The concern is whether chemically treated waters are "marsh ready," that is of acceptable quality to be discharged to the marshes of the Everglades ecosystem.

The marsh readiness of water from the test cells was evaluated using a set of ionic parameters presented using Stiff diagrams, Schoeller plots, and radial plots. Pre-treatment period parameter value averages were compared to treatment period parameter values for the NTCs and STCs, and available water quality data for the Water Conservation Areas (WCAs).

Pretreatment and treatment period Stiff diagrams for the cells were very similar. Increased iron and chloride levels from the treatment period Fe cell was the only clear difference. Both pre treatment and treatment period Stiff diagrams were very similar to that of the WCA-2A site, and least similar to the Stiff diagram of an interior site in the Loxahatchee Refuge. Diagrams of average values of ionic constituents for the six test cells for the pretreatment period August 1999 through January 2000 are very similar. The north site cells (NTCs) appear to have a slightly higher iron component values but the overall patterns are quite similar. Comparison of the calibration period diagrams with treatment period diagrams shows that treatment had little effect on ionic balances and ratios. A cell by cell comparison for the last two quarters shows similar patterns to the ionic signature in both quarters.

A comparison of the test cell data with data from the Water Conservation Areas is a useful method of extending the comparison to consider the question of overall "marsh readiness" of the water. The three plots comparing the WCAs show that constituent concentrations differ between the respective conservation areas. Comparison of the MWTS test cells treatment period data with WCA data suggests that the ionic condition of test cell's effluent is very similar to that found in the interior of WCA 2. The exception is NTC-2, the iron treatment.

1.2 General Conclusions

- Water Regime—The hydrologic targets (depth and hydraulic loading rates) for the wetland cells were met throughout the quarter (Section 4.2).

- Water Balance—Water balances close if outflows are calculated by difference (Section 4.2.3).

- Water Quality—Concentrations of phosphorus and nitrogen decreased across the NTC systems from inflow to outflow, with experimental treatment system decreases far exceeding the control cell decreases. For the STCs the treatment effects are less clear (Section 4.4).

- Mass Balance—TP mass balances clearly showed the effect of chemical treatments in the NTCs, and the treatments clearly had different effects, with aluminum treatment showing the greatest removal rates (Section 4.5).

- Marsh Readiness – Stiff, Schoeller, and Radial Plots were used to compare ionic constituent data sets from the pre-treatment period to treatment period data, and both data sets to interior sites in the Water Conservation Areas. Experimental and control data diagrams were very similar to WCA-2A interior site diagrams (Section 6).

2.0 Purpose

The South Florida Water Management District (District) is conducting research focused on potential advanced treatment technologies to support reduction of phosphorus loads in surface waters entering the remaining Everglades. Particular focus is being placed on the treatment of excess surface waters from the Everglades Agricultural Area (EAA) as well as Lake Okeechobee water that is diverted through the primary canal system to the Lower East Coast of Florida.

Federal- and State-level Everglades restoration efforts are focused on addressing two programmatic factors: reduction of stormwater-based phosphorus (P) loading to the Water Conservation Areas (WCAs)/Everglades National Park, and promotion of sheet flow through the system. The Everglades Forever Act (EFA) mandates an interim performance standard of producing treated waters with total phosphorus (TP) concentrations of 50 parts per billion (ppb) or less. However, this may not be low enough to prevent alteration of the aquatic and wetland ecosystems downstream in the remaining Everglades; ongoing research and an anticipated, formal rulemaking process will seek to define what will be the ultimate TP standard.

The Managed Wetlands Treatment System (MWTS) evaluation was authorized in November 1998. The objective of this research (Phase I) is to identify preferred technologies that should be designed and implemented full-scale to optimize treatment performance of the cattail-based Stormwater Treatment Areas (STA) during Phase II of the State's Everglades Construction Program (ECP).

Sampling at the ENR Test Cells began in the first week of July 1999 under the baseline sampling period. The baseline calibration period ran through the beginning of February 2000. During the calibration period, untreated source water was being discharged to both the North and South Test Cells.

Chemical treatment of source water with either ferric chloride or an aluminum chloride compound was instituted during the third quarter in three cells, two treatments in the north test cell site and one treatment in the south test cell site. An additional cell in each location serves as a control. The chemical treatment period is scheduled to run for 12 months through February 2001.

It should be noted that the information contained in this document remains preliminary and draft. Complete quality control (QC) review of all data sets has not been conducted on all of the information being transmitted because some of it was only recently received from the various analytical support laboratories and some data sets for this quarter have yet to be completely reported by those laboratories. This document is an interim report prepared under Task 2 of the MWTS study program contract held by CH2M HILL. It provides a brief summary of progress as it relates to data collection, on the MWTS Research Project during the fifth quarter (July - September 2000).

Exhibit 2-1 provides a plan view of a typical MWTS Test Cell showing sampling locations and walkways.

3.0 Meteorological Data

3.1 Solar Radiation

Solar radiation is being continuously monitored by CH2M HILL at the South ENR STRC using a pyranometer and phostosynthetically active radiation (PAR) quantum sensor. Exhibits 3-1 and 3-2 illustrate total solar radiation and PAR, respectively, at this site for the first five quarters. PAR and total insolation monitored during this quarter averaged 28.61 Einstein per square meter per day (E/m²/d) and 18.51 megajoules per square meter per day MJ/m²/d, respectively. Average total insolation and PAR both exhibited a decrease from last quarter.

EXHIBIT 3-1
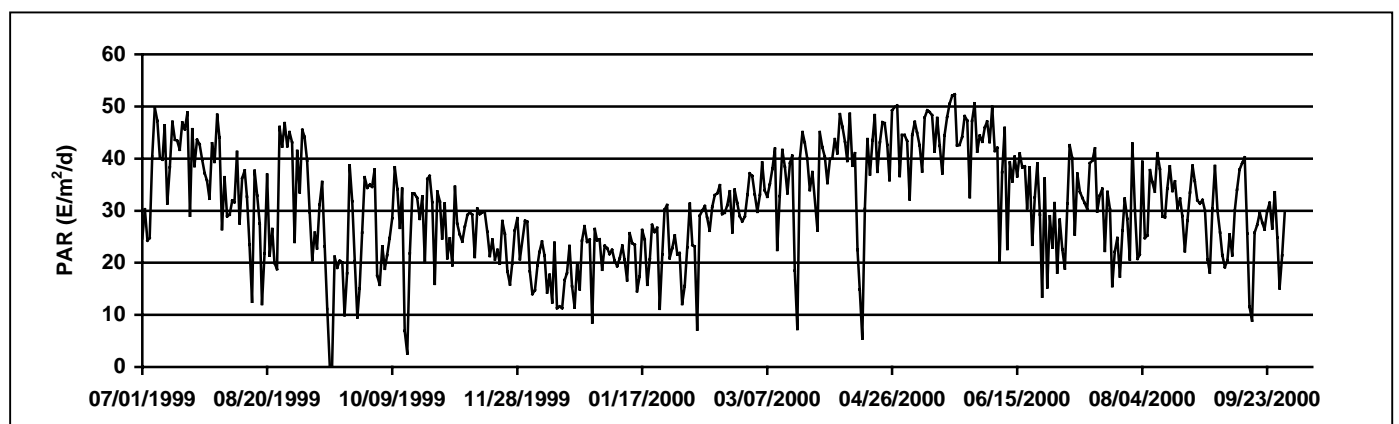*Total Solar Radiation Measured at the South ENR STRC*
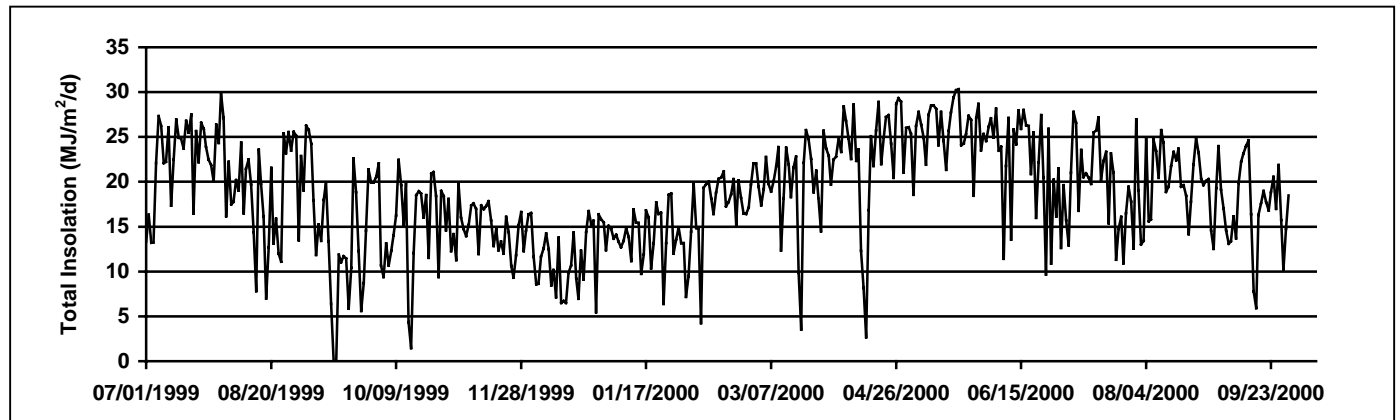
EXHIBIT 3-2
Photosynthetically Active Radiation Measured at the South ENR STRC

3.2   Air Temperature

On May 29, 1999, CH2M HILL initiated continuous monitoring of air temperature. An air temperature probe is mounted along with the solar radiation equipment at the South ENR STRC. Air temperature averaged 21.44, 24.69, and 25.85 degrees C during the April, May, and June study periods, respectively. Exhibit 3-3 presents average, maximum and minimum air temperatures recorded at the South ENR STRC.

3.3   Rainfall

Daily rainfall data were provided by the District from ENR Rainfall Stations ENR301 (South) and ENR101 (North). Exhibit 3-4 illustrates daily total rainfall at each ENR Rainfall Station for the July 1999 through June 2000 study period. Rainfall during this quarter totaled 1.24 inches at the North Station and 7.03 inches at the South Station. Most of the quarterly difference in rainfall quantities between the two sites is attributable to April precipitation: there was approximately 4.2-inches more rainfall measured at the South site in April compared to the North site.

3.4   Evapotranspiration

Daily evapotranspiration (ET) data were provided by the District. Exhibit 3-5 illustrates daily total ET at the ENR Evapotranspiration Station ENRP for July 1999 through September 2000.

4.0 MWTS Test Cells

4.1   MWTS North and South Test Cells

4.1.1   General Features

Exhibit 4-1 provides a general design summary of the MWTS Test Cells being monitored at the North and South MWTS Test Cells.

Exhibit 4-1
General Design Summary of the MWTS Test Cells

Site	Cell	Substrate	Target Water Depth (cm)	Target HLR (cm/d)	Treatment
North (NTC)	2	Peat	33	10.0	Ferric Chloride
	3	Peat	33	10.0	Control
	4	Peat	33	10.0	Aluminum Chloride
South (STC)	5	Peat	33	10.0	Control
	6	Peat	33	10.0	Control
	7	Peat	33	10.0	Aluminum Chloride

4.1.2   Operation of Chemical Treatment Units at ENR

Chemical treatment at the ENR site began on February 16, 2000 with the startup of the north aluminum pilot plant. Exhibit 4-2 summarizes the chronology of pilot plant operations. Target flow rate to the plant was started at 30 gallons per minute (gpm) for the first week, and was then increased to 37 gpm, which has been the target flow rate for all plants. The target flow of 37 gpm yields a hydraulic loading rate of 4 in/d (10 cm/d) to the wetland cells (incremental rate of 1 ft/d at the 1/3 sampling point in the cells). On November 10, 2000 the flow rate was reduced by 25% to 28 gpm to facilitate improved floc settling in the clarifiers and reduce inflow TP concentrations.

EXHIBIT 4-2
Chronology of MWTS Pilot Plant Operations at the ENR

2/16/00	Started up north aluminum plant. Water flow was 30gpm. PACl dose was 1.5 equivalents. Cytec N-1986 emulsion polymer was dosed at 0.5 mg/L.
2/22/00	Started up iron plant.
2/29/00	Established target 37 gpm water flow at north plants
3/2/00	First wasted solids in iron plant
3/8/00	Began wasting 200 gallons/day in iron plant
3/17/00	Increased iron plant wasting to 300 gpd
3/17/00	Started up south aluminum plant.
4/17/00	First wasted solids in north aluminum plant
5/1/00	Began wasting 200gpd in north aluminum plant
5/3/00	Began 3-day on-site evaluation and jar testing. At the north aluminum plant, PACl dose was increased to 3 equivalents and polymer dose was increased to 1 mg/L. FeCl3 dose was increased 50% to 2.25 equivalents and polymer dose was increased 50% to .71 mg/L.
5/5/00	Switched to dry polymer, Cytec Superfloc A-130, at the north plants. Maintained new dosages.
5/6/00	South aluminum plant PACl dose was increased to 3 equivalents. Polymer dose was increased to 1 mg/L.
5/8/00	Switched to 1 mg/L dose dry polymer, Cytec Superfloc A-130, at the south aluminum plant . Began wasting 200gpd at same.
5/9/00	Increased iron plant wasting to 400 gpd.
6/10/00	Iron plant coagulant dose was increased to 3 meq/L. Aluminum plants' PACl dosage increased to 3.75 meq/L.
7/12/00	Installed 500gal sludge transfer tanks and 100gal polymer tanks to help reduce labor requirements with higher chemical feed rates.
7/15/00	Reduced monitoring frequency to 3 days/week.
9/6/00	Stopped recirculating solids.
9/8/00	Returned coagulants to a 1.5 meq/L dose. Returned polymer to a 0.5 mg/L dose
10/16/00	Began using FeCl3 from another vendor
11/10/00	Reduced water flow rate by 25% to 28gallons per minute (gpd).

A polyaluminum chloride product, HyperIon 1090, has been used since startup as the aluminum coagulant at the North Aluminum plant. The starting target dose was 1.5 meq/L.

The initial polymer used was an anionic emulsion, Cytec N-1986, added at a dose of 0.5 mg/L.

On February 22, the iron plant was started up at the North ENR site, using ferric chloride at a dose of 1.5 meq/L. Polymer type was Cytec N-1986 at a dose of 0.5 meq/L. Caustic is added to this plant to maintain pH in the coagulant addition zone of approximately 7 to 7.5 SU as previously determined from jar tests.

The aluminum plant at the south test cells was brought online the following month, with identical dosing used at the north beginning on March 17. For each plant, there was a two to three week debugging period during which target water and chemical flow rates were confirmed.

All three of the plants were operated with sludge recirculation from the plate settler to the flocculation zone from startup through the first week in September. Since the first week in September, however, the systems have been operated as once through systems (SRT = HRT), with no recirculation.

4.1.2.1 North Test Pilot Evaluation

Following a roughly ten week operating period, a series of tests was conducted at the north pilot plants between May 3rd and 5th. The testing was conducted in response to laboratory results that indicated pilot plants were not yielding P removals expected based on jar tests. Thus, there was an interim conclusion that either the plants were not operating as expected, or that the water matrix had changed significantly from when the jar testing was conducted. The testing protocols were established by Luke Mulford and Paul Steinbrecher. Tests and evaluations were carried out under Dr. Mulford's direction. The main objectives of this focused testing were (1) to determine what process modifications could be implemented to reduce total dissolved phosphorus (TDP) concentrations in the plant effluents, and (2) to reduce solids carry over from the plate settlers.

The following steps were taken to address excessive floc overflow:

- Chemical addition points were adjusted to maximize chemical dispersion
- Floc formation was assessed and slightly improved by modifications to the mixing regime
- Hydraulic loading rate was verified by direct measurement of the plates
- Chemical dose rates and calibration procedures for measuring feed rates were checked and verified as correct
- Evaluations were made on various combinations of coagulant and polymer dose rates
- Two additional polymers were evaluated
- Settling characteristics were evaluated to determine if hindered settling was occurring

The excessive TDP concern was addressed by verifying sample collection procedures and testing possible pass-through by testing filtered and unfiltered fractions. In addition, possible feedback from the sludge storage tank was tested by comparing samples from the iron plant clarifier with the plant's effluent and coagulant samples were tested for contamination.

Conclusions drawn from the focused testing effort were:

1. At a coagulant dose of 1.5 meq/L (13.5 mg/L Al, 27.9 mg/L Fe) the TDP was not reduced below the 10 µg/L target immediately after the clarification process.
2. The TDP concentration of the solids storage tank effluent was not significantly different from the clarified samples indicating that feed back from the sludge was not occurring.
1. High solids did not appear to effect TDP after filtering (no discernable P bearing solids appear to pass the 0.45 µm filter.)
4. The dissolved residual metals concentration indicated that the coagulation process was relatively efficient.
5. The coagulants had measurable amounts of TDP ranging from 5 to 10 µg/L P at a dose of 1 meq/L (9 mg/L Al, 18.6 mg/L Fe)
6. Increasing the coagulant doses resulted in a measured TDP of 12 µg/L P. While this concentration was a historical low for the pilot units it was not clear that the increase in coagulant dose resulted in the reduction of TDP.

The following recommendation for future course of actions were made at that time:

- Consider reducing sludge age
  - To promote flocculent settling
  - Extended sludge age did not appear to be providing excess P adsorptive capacity
- Continue to test the (dry) A130 polymer product which was effective for CT/SS.
- Verify that coagulants are free from contaminants
  - Submit serial dilutions
- Split samples among several laboratories to evaluate laboratory reliability

4.1.2.2 Changes Made After North Test Pilot Evaluation

On May 3, the PACl dose at the north aluminum plant was doubled to 3 meq/L and the FeCl3 dose was increased by half to 2.25 meq/L, and polymer dose was doubled at the aluminum plant to 1 mg/L and increased roughly 50% at the iron plant to 0.7 mg/L. On May 5, we switched to the dry polymer product that was effective on the CT/SS project and continued dosing at the new rates.

On May 6, the same dose increase at the north aluminum plant was applied to the south plant. Two days later, on May 8, the switch to dry polymer was implemented at the south. One month later, on June 10, seeing little improvement in the TDP data, the iron coagulant dose was again increased to 3 meq/L. The aluminum plants' coagulant dose was increased to 3.75 meq/L.

To more fully utilize automatic sludge wasting and to improve the practicality of polymer addition at the higher dose rates, 500gal solids transfer tanks were installed on July 12 and the 100gal tanks were transferred and cleaned for polymer makeup and storage. With these hardware changes in place, the plants could be operated with less time onsite for making up chemicals. On July 15, the onsite monitoring frequency was reduced to three days per week.

4.1.2.3 Laboratory Problems

By early July it was clear that even with the operational adjustments made in May and June, the pilot plants were still not producing the low levels of TDP that were expected, even at

extremely high coagulant doses. Some of the laboratory data were questioned by this time. Laboratory problems included chronically reporting dissolved fractions greater than total fractions, chronically rerunning analyses, and late delivery of results. At this point several other researchers were also beginning to call into question their results run by this lab for other studies.

On July 10, diluted samples of iron and aluminum coagulants were prepared and split between the original contract lab (PPB), and another lab that has run P samples for two other advanced treatment technology (ATT) projects (submerged aquatic vegetation (SAV) and chemical treatment with solids separation(CT/SS)). From this screening level evaluation, it became clear that:

- The iron coagulant was contaminated with a soluble organic phosphorus

- The aluminum coagulant was not contaminated

- The accuracy of the original contract lab's data appeared questionable based on anomalous results from the dilution series tested, relative to the other labs results.

Since the time of that screening evaluation, there has been continued and repeated evidence that the contract lab cannot reliably measure TP and TDP at low concentrations (<10 to perhaps 20 ppb or so). Among the observations are splits of over 500 samples that another ATT group (PSTA) conducted using IFAS labs and PPB labs. In that analysis the average TDP reported by PPB was typically twice the value of that from IFAS labs (see Appendix E). The iterative receipt of multiple versions of preliminary data sets (reruns) was a chronic problem for the PSTA group as well, and thus they switched back to IFAS labs from PPB.

In response to increasing criticism from reviewers that the MWTS chemical treatment technology was not "working", we switched from using PPB for the primary P series measurements to using DB labs on September 6, 2000. Since that time, we have continued to split a number of samples with the original lab, PPB, and continue to use PPB labs for other (non-P) analyses The PPB lab splits continue to be reported with anomalies that require multiple reruns, and are typically substantially higher than the DB data. Thus, the DB data have been reported on the data tables and on the graphs since September 6.

Since the time of the laboratory switch, many of the chemical plant effluent TDP samples are now being reported at less than 10 ppb. Despite dramatic reductions in effluent TSS from the plants since recirculation was stopped in early September, effluent TP results are typically in the 30 to 50 ppb range at the North plants, and around 20 ppb at the South plant. This may be an artifact of floc carryover from the sludge storage tanks, rather than an indication of the TP leaving the plate settlers. To better evaluate this, we began taking grab samples from the plate settlers on November 8 for TP and TSS on the same days that composite samples are being taken from the normal effluent sampling points on the solids storage tanks. There have been five such collections to date. The results of the first three are inconclusive. There is no clear indication of a significant difference in either TP or TDP between the two sampling locations. Results through November 29 remained in the same range.

With the change from one lab to the other, coagulant doses were once again reduced to the original levels (1.5 meq/L), and recirculation was discontinued. As discussed previously,

this has significantly reduced effluent TSS from the plate settlers, with no discernable reduction in TDP removal. One final change made was a switch in iron coagulant suppliers from Kemiron to Apperson Chemicals on October 16. Apperson is the company that supplied "clean" iron coagulant to the CT/SS program last winter. Results of lab tests on a dilution series of this coagulant showed P contamination. One meq of 40.5% FeCl3 contained .007 mg/L TP and .008 mg/L TDP, two meq yielded .015mg/L TP and .014 mg/L TDP and three meq yielded .021 mg/L TP and .

4.1.2.4 Summary

In terms of phosphorus removal the chemical plants are operating as expected from earlier jar testing (using the District Lab for analysis), with the capture of a majority of the influent TP in a hydroxide floc and TDP concentrations typically less than 10 ppb. It is probable that this has been the case throughout most of the study, although erroneous lab data have prevented us from documenting this, or from seeing the effect of operational changes over time.

TP concentrations are higher than the desired target of 10 ppb from the chemical plants due to phosphorus in unsettled floc. An evaluation of the TP concentration leaving the plate settlers is underway, and we will know soon whether a reduction in particulate is realistic or not. We have also replaced the iron coagulant with a "clean" source.

4.2 Water Regime

The MWTS water regime includes the components of water depth, hydraulic loading rate, and water mass balance. Exhibit 4-3 summarizes the MWTS Test Cell water regime data for this quarter and previous quarters. Water level, inflow, outflow, and hydraulic loading rate (HLR) time series charts are presented in Appendix A.

4.2.1 Water Depth

Water level measurements in the MWTS Test Cells were recorded at the District staff gauge near the outflow of each Test Cell. Readings were taken weekly or more frequently. Daily average stage data were provided by the District for the North and South MWTS Test Cells. The target operating depth for the Test Cells is 0.33 m. For the fifth quarter the average cell depth was within 0.15 m of the target level in all cells.

4.2.2 Hydraulic Loading Rate

The HLR, q, is calculated using the following equation:

$$q \ (m/d) = Q/A \hspace{4cm} \text{Equation 1}$$

Where:

Q = volumetric flow rate (m^3/d)

A = wetted area of the cell (m^2)

Daily average water inflows to the MWTS Test Cells are based upon the inlet splitter box at each site.

The target HLR for MWTS testing at the ENR is for the quarter was in the range of 8 to 10 cm/d. Actual average HLR in all cells in this quarter ranged from 7.8 to 10.0 (see Exhibit 4-3).

4.2.3 Water Balance

Exhibit 4-4 summarizes the water balance in each cell. The general balance between water storage, inflows, and outflows is shown in Equation 2:

$$\Delta V = V_{in} - V_{out} + P - ET - S \hspace{3cm} \text{Equation 2}$$

Where:

ΔV = change in storage volume
V_{in} = inflow volume
V_{out} = outflow volume
P = precipitation
ET = evapotranspiration
S = seepage

Because the Test Cells are lined and seepage is assumed to be zero, the water balance equation can be re-arranged as shown in Equation 3:

$$V_{in} - V_{out} + P - ET - \Delta V = 0 \hspace{3cm} \text{Equation 3}$$

At the conclusion of the baseline period (Q1 and Q2) a water balance for each test cell was developed (see 2nd Quarterly Report). In that analysis inflow and outflow balanced for only one of the six test cells, NTC 3. The high positive and negative residuals for the other five test cells indicated variation in one or more outflows and storage in response to a variety of factors. Over the course of the baseline period, water balance residuals were expected to become relatively small. The project team implemented a quality control plan for field data collection. Some of the steps include the following: 1) less frequent adjustment of weir height in water level 2) careful measurement of weir height setting, and 3) verify that our measurement of flow over the weirs is accurate. In addition we assessed the value of calculating the water balance on a daily basis rather than on a monthly average. The water balance calculations for Q1 and Q2 indicated that the magnitude of the residuals remain high.

Due to the uncertainty in estimating outflow from the weir setting Equation 3 has been utilized to calculate the outflow by difference from the end of Q2 through the present quarter (see last set of columns in Exhibit 4-4).

4.3   Field Parameters

Field parameters (water temperature, pH, dissolved oxygen [DO], percent saturation, total dissolved solids [TDS], and specific conductance) were measured in the MWTS Test Cells biweekly at the splitter box for the raw water inflow, the point of discharge from the pilot plant into the marsh (Plant Effluent - PlntEff), two internal sampling points (1/3 and 2/3 monitoring walkways) and test cell outflow. Exhibit 4-5 depicts (in a simple schematic drawing) the sampling locations and water flow path.

Exhibit 4-6 summarizes the monthly averages for field parameter data during this quarter and for previous quarters. Averages were calculated from mid-depth measurements taken in the Head Cell and Test Cells. Additional graphical summaries of these parameters in Appendix B, temporal trend charts, and Appendix C, water quality gradients.

Temperature was relatively uniform across the head cell and Test Cells at the North and South (Exhibit 4-6) ENR sites. Certain field parameters were affected by the chemical treatments. Relative to the raw water inflows pilot plant effluents had generally higher specific conductance, TSS and dissolved oxygen (DO). Monthly average [TDS] in NTC2 (Fe treatment) was higher than the average inflow concentrations and higher than NTC4 (Al treatment) outflows.

4.4   Water Quality Data

Chemical Treatment Units

Two chemical treatment units at the north site (NTCs) (ferric chloride – NTC 2 and poly-aluminum chloride – NTC 4) and one treatment unit at the south site (poly-aluminum chloride, STC 7) operated for the entire quarter. The plants have been operated with a target flow rate of 37 gpm (202 m^3/d), which yields a hydraulic loading rate of 10 cm/d to the wetland cells. Dosing rates remained at approximately 27 mg/L (3 meq/L) Al at the North (NTC-4) and South (STC-7) aluminum plants, and 42 mg/L (2.25 meq/L) Fe at the North (NTC-2) iron plant until early September (see previous discussion in Section 4.1 and Exhibit 4-2).

General Water Quality Results

At both north and south MWTS cells raw water inflows were sampled at the respective inflow splitter boxes mounted on one of the pilot plants at each site. Water coming from the Head Cell enters the splitter box, which is connected to pipes going to each wetland cell. The splitter box sends an equal amount of water to each of the cells to which it is connected. Water quality sampling for Q5 followed the routine schedule and protocols detailed in the MWTS research plan. STC 5, one of the two southern site control cells, was dropped from the general sampling regime at the end of Q4, since the statistical analysis of the baseline period showed that STC 6 was the preferred control (see analysis in 2nd Quarterly Report). The information collected from and calculated for STC-5 through Q4 continues to be shown in the several tables and figures of this (Q5) report but STC 6 data has become the sole control cell for comparison with STC-7.

The sample data thus collected were used to characterize inflow and outflow to all cells at each site, respectively. Samples were also collected from the effluent of each pilot plant (PlntEff), internal wetland sampling points, and the outflow of each test cell at varying frequencies. Phosphorus samples were collected at the highest frequency and were analyzed for a number of phosphorus forms. Test Cell raw water inflow, plant effluent (marsh inflow), internal sampling points (1/3 and 2/3 station) and wetland test cell outflow samples were collected biweekly for analysis of total phosphorus (TP), total dissolved phosphorus (TDP), and soluble reactive phosphorus (SRP). From the collected phosphorus data, total particulate phosphorus (TPP) was estimated by the difference: TP - TDP, and dissolved organic phosphorus (DOP) was estimated by the difference: TDP - SRP.

Test Cell inflows, plant effluent, internal 1/3 sampling stations and outflows were sampled monthly for total nitrogen (TN), total Kjeldahl N (TKN), total ammonia N (NH_3-N), nitrate +nitrite N (NOx-N), calcium, total suspended solids (TSS), alkalinity, total organic carbon (TOC), total dissolved solids (TDS), color, chloride, sulfate, hardness, aluminum, magnesium, iron, silica, and turbidity. From the collected nitrogen data, organic nitrogen was estimated by the difference: TKN - NH_3-N.

Monthly average values for water quality data collected from July 1999 through September 2000 are presented in Exhibit 4-7. Temporal trend charts comparing inflow versus outflow concentrations for TP, TPP, and TDP in each test cell are provided in Exhibits 4-8 through 4-13. Additional data summaries are provided in the appendices; included are inflow and outflow time series charts for parameters (Appendix B) and time series charts for water quality gradient through the wetland cells (Appendix C). In Appendix B reported outlier values were identified only as points off the graph (e.g. see Nitrite/Nitrate Nitrogen Concentrations) in order to provide a reasonable viewing scale for the rest of the data set. Either these points were verified but continue to be considered outliers or are still being re-tested. The MWTS database also includes pre-July 1999 water quality data collected by the District in the north and south test cells. The District initiated sampling in September 1998 for NTC and November 1998 for the STC. The pre-MWTS data are included in the time series plots, Appendix B.

Several patterns of parameter behavior are evident from this quarter's and earlier data relative to a comparison of the inflow and outflow concentrations, assuming that under average conditions inflows roughly equal outflows. These general trends are provided by

parameter for the North and South Test Cells in Exhibit 4-14, the summary includes results for Q1, Q2, Q3, Q4, Q5 and for the pre-MWTS monitoring (QO) where available.

Results, generally comparing constituent concentration of the raw inflow with test cell outflow, from the northern and southern ENR sites are as follows:

- Fe and Al treatments reduced TP, TPP, SRP, TDP, DOP, TN, TKN, org-N, and TOC concentrations relative to the respective control. Color was reduced in both Al treatments.

It appears that the wetland contributed TDP over the period of pilot plant operation (control cell results) but overall the treatment cells demonstrated net TP removal (NTC 2 and NTC 4), or little net change (STC 7)

- TPP in the pilot unit effluent was removed in the wetland.

These trends are generally consistent with those observed in the previous quarter (Q4).

Phosphorus

In the fifth quarter control cell NTC3 raw water inflow TP concentration was greater than that from the wetland outflow (Exhibits 4-7, 4-8, 4-9, and 4-10). This trend was often reversed for the control cells STC5 and STC6 (Exhibits 4-7, 4-11, 4-12, and 4-13). For both locations inflow TP was relatively evenly split between particulate and dissolved fractions.

Raw water influent [TP] was in a range of 90 to 230 ppb at the NTCs and 30 to 180 ppb at the STCs. These ranges are very similar to the immediately previous quarter (Q4) and represent an increase over previous quarters for both sites. NTC treatment wetland outflow TP concentrations were lower for the treatments compared to the control. Iron treatment resulted in a 50-70% reduction and aluminum a 50-85% reduction. The [TP] and [TPP] concentrations fall across the length of the wetland. This result indicates that particulate P from the respective chemical treatment effluent was removed at the head of the wetland. The treatment effect on wetland outflow is evident in the time series (Appendix B) and wetland water quality gradient plots (Appendix C).

At the southern ENR location outflow [TP] was 10% to 20% lower for the aluminum treatment versus control cell STC6.

At both sites the internal 1/3 station exhibited relatively higher concentrations for TP, TPP, and TDP in all three test cells. This appears to be the result of surficial sediment entrained from the sediment-water interface in the sample, and thus these samples are not truly representative of the undisturbed water column. For the two aluminum treatments (NTC4 and STC7) water samples form the 1/3 station contained aluminum hydroxide floc that had carried over from clarifier and then settled in the wetland. The field sampling routine has been modified to assure that the water column not the sediment-water interface is sampled.

Exhibit 4-14
General Water Quality Trends for Inflow Versus Outflow Concentrations for North and South Test Cells

Parameter	General Trend for Inflow vs. Outflow Concentration					
	Inflow ≥ Outflow		Inflow = Outflow		Inflow ≤ Outflow	
	North	South	North	South	North	South
Phosphorus						
Total P	Q0, Q1, Q2, Q3, Q4, Q5	Q2		Q0, Q4, Q5		Q1, Q3
Total Particulate P	Q1, Q2, Q3, Q4, Q5	Q2		Q5		Q1, Q3, Q4
Total Dissolved P	Q1, Q2, Q3, Q4, Q5	Q3		Q4, Q5		Q1, Q2, Q4
Soluble Reactive P	Q1, Q2, Q3, Q4, Q5			Q1, Q2, Q3, Q4, Q5		
Dissolved Organic P	Q2, Q3, Q4, Q5		Q1	Q1, Q3, Q4, Q5		Q2
Nitrogen						
Total N	Q0, Q1, Q2, Q3, Q4, Q5	Q0, Q3, Q5		Q1, Q2		
TKN	Q0,Q1, Q2, Q3, Q4, Q5	Q5		Q0, Q1, Q2, Q3, Q4		
Nitrate & Nitrate N	Q0	Q0, Q1, Q2, Q3,Q4	Q1, Q2, Q3, Q4, Q5	Q5		
Ammonia N	Q1, Q2, Q3, Q4, Q5	Q1, Q2, Q3, Q4, Q5				
Organic N	Q4, Q5	Q5	Q1, Q2, Q3	Q1, Q2, Q3, Q4		
Total Organic Carbon	Q4, Q5	Q5	Q0, Q1, Q2 Q3	Q0, Q1, Q2, Q3, Q4		
Total Dissolved Solids	Q5	Q5	Q1, Q2,Q3, Q4	Q0, Q1, Q2, Q3, Q4		
*Total Suspended Solids		Q0	Q0, Q1, Q2, Q3, Q4, Q5	Q1, Q2, Q3, Q4, Q5		
Color	Q4, Q5	Q5	Q1, Q2, Q3	Q1, Q2, Q3, Q4		
Chloride			Q0, Q1, Q2, Q3,Q5	Q0, Q1, Q2, Q3, Q4, Q5	Q3*, Q4*, Q5*	
Sulfate	Q1, Q4, Q5	Q1, Q2, Q4, Q5	Q2, Q3	Q0, Q3		
Alkalinity	Q0, Q3	Q0, Q3, Q4, Q5	Q1, Q2, Q4, Q5	Q1, Q2		
Hardness	Q5	Q0, Q1, Q3, Q4, Q5	Q1, Q2, Q4	Q2	Q3	
Aluminum	Q3	Q0, Q3*	Q4, Q5	Q1, Q2, Q4, Q5	Q1, Q2	
Magnesium			Q1, Q2, Q3, Q4, Q5	Q0, Q1, Q2, Q3, Q4, Q5		
Calcium	Q5*	Q0, Q1, Q3, Q4, Q5	Q1, Q2, Q3, Q4	Q2		
Iron	Q1, Q2, Q3, Q4*, Q5	Q3		Q0, Q1, Q2, Q4, Q5	Q3*Q4*, Q5*	
Silica	Q4, Q5	Q4*, Q5	Q1, Q2, Q3	Q1, Q2, Q3		
Turbidity	Q5		Q1, Q2, Q3, Q4	Q1, Q2, Q3, Q5		Q4

* Strongly cell dependent

Phosphorus Species

Chemical analyses provide a breakdown of TP into total particulate P (TPP), total dissolved P (TDP), dissolved organic P (DOP) and soluble reactive P (SRP). A summary of each P-species is as follows:

- TPP—raw water influent TPP levels at NTCs were typically greater than or equal to levels at STCs (Exhibits 4-7, and 4-8 through 4-13 and time series charts in Appendix B). Water quality gradient data (Appendix C) show treatment effect on wetland outflow [TPP] for the fifth quarter. Outflow TP concentration was higher for the control (NTC3) relative to the chemical treatments (NTC2 and NTC4). As noted above, for the treatment period, [TP] and[TPP] drop across the wetland for both chemical treatment cells at the north site. For the quarter the northern treatment cells had inflow [TPP] in the range of 60 to 80 ppb. Monthly average outflow TPP concentration was 20 to 39 ppb for the iron treatment and the control, but averaged 12 ppb for the aluminum treatment. For the STCs, inflow [TPP] averaged 30ppb. The outflow concentration for the control cell was equal to or higher than the inflow; in contrast, the outflow concentration for the aluminum treatment averaged 20 ppb.

- TDP—NTC control cell (NTC 3) and treatments (NTC2 and NTC4) had lower outflow TDP concentrations as compared to inflow values. The average outflow [TDP] (= 15 ppb) for the two treatments (Fe and Al) were lower than the control outflow concentrations, which averaged 30 ppb. The effect of treatment is apparent at the NTCs with significant reductions in [TDP] compared to the control (Exhibit 4-7, 4-8, 4-9, and 4-10, and time series charts in Appendix B). For the STCs the monthly wetland influent [TDP] average ranged from 14 to 56 ppb and the wetland effluent ranged from 15 to 56 ppb. For the STCs there was no clear chemical treatment effect for this parameter.

- SRP—Influent [SRP] rose steadily at the northern site for the quarter from approximately 18 ppb at the start to 115 ppb at the close. Influent [SRP] was higher at NTCs compared to STCs (averages of 45 ppb versus 11 ppb). At the southern site outflow [SRP] is typically less than 10 ppb for all three test cells. Outflows from the NTCs (treatments and control) averaged less than 10 ppb. [SRP].

Nitrogen

The average Q5 raw water inflow [TN] was slightly lower for STCs as compared to NTCs (3.05 mg/l for NTC and 2.71 mg/L for STC) (Exhibit 4-7). At both locations the inflow and outflow TN values are approximately equal for the control cells (NTC3, STC6). NTC and STC results show a treatment effect with lower wetland effluent [TN] for the treatments as compared to the controls. (Exhibit 4-7, Appendix B). At the NTCs the aluminum treatment reduces nitrogen to a greater extent than the iron.

Other Water Quality Parameters

For several of the remaining parameters the inflow and outflow concentrations are approximately equal at the respective test cells (Exhibits 4-7 and 4-14). Included in this group are TSS, magnesium, and aluminum. Other observations for water quality trends in Q5 include:

- TDS—NTC2 (Fe treatment) outflow [TDS] was distinctly higher than the average inflow concentrations while for the Al treatments (NTC4, STC7) the outflow [TDS] was slightly lower.

- Total Calcium—NTC2 (Fe treatment) outflow had distinctly lower total Calcium concentrations that of the cell inflow or control cell outflow. NTC4 and STC7 (Al treatments) were very similar to their respective control cell for average total calcium concentration.

- Sulfate—NTC Treatments (both Fe, Al) slightly reduced outflow sulfate concentrations compared to the control, in NTC2 and NTC4. Comparison of STC6 and STC7 were less clear.

- Color—Chemical treatments at both the northern and southern sites reduced color relative to the control. At the north site, the Al treatment resulted in lower color values than the Fe treatment. The control treatments at both sites had little apparent effect on color.

- TOC—Results for the fifth quarter are similar to those for color, the chemical treatments at both locations resulted in lower outflow [TOC], compared to the controls. At the north site the Al treatment resulted in lower TOC values relative to the iron treatment. A single date showed outlier values for [TOC] in NTC 4, STC6, and STC7. The analytical quality assurance process verified the value and the aberrant result was likely caused by a sampling error.

- Dissolved silica—Results follow the pattern noted for color and TOC, reduced concentration for outflow as compared to inflow for Al and Fe treatments.

- Fe, Cl—The ferric chloride treatment (NTC 2) resulted in higher outflow concentrations of iron and chloride than the either the control or the aluminum treatment. At the remaining test cells the inflow and outflow values are approximately equal for iron and chloride.

- Hardness—Average NTC outflow hardness tended to be slightly lower than the average inflow value. The trend was most pronounced in the Fe treatment (NTC2). No trend was discernable in the STCs.

- Alkalinity. —The alkalinity inflow/outflow relationship varied by sample date in all cells except STC7 (Al treatment) where outflow alkalinity was distinctly lower than that of the inflow.

- Turbidity—All NTC cells displayed lower average outflow turbidity compared to the inflow values. STC6 (southern control cell) showed higher average outflow turbidities, while STC7 outflow turbidities were very similar to the inflow values.

4.5 Mass Balances

For this project nutrient removal performance is most meaningfully quantified by calculating a mass balance; comparing the total mass of a nutrient that enters a system from the total mass that leaves a system. For example, phosphorus removal (through physical,

biological, and chemical processes) can be estimated simply as the difference between these loads. As an assessment of MWTS performance, mass balances were estimated for each of the Test Cells. Mass balance estimates utilized the water balance calculated by the difference method using Equation 3.

Mass balance for P and N species were calculated on quarterly (Exhibit 4-15) and monthly intervals (Exhibit 4-16). These summaries were generated using weekly mass balance calculations, hence, only weeks when surface water samples were collected were included in calculating monthly averages. Contributions of rainfall to phosphorus and nitrogen loads to the Test Cells were not included in these mass loading estimates. Preliminary estimates indicate that rainfall load may make up between 1 to 10 percent of the total load. Final mass balance analyses for this project will include estimates of rainfall contribution to TP and TN.

Several patterns of parameter behavior are evident from the Q5 data regarding removal rates for phosphorus and nitrogen based on mass balances. The patterns are as follows:

- Inflow was greater than outflow—the wetland system was reducing or converting the influent load

- Inflow was approximately equal to outflow—the wetland system was having no significant effect on the influent load

- Inflow was less than outflow—the wetland was exporting of the constituent.

The mass balance trends are provided in Exhibits 4-17 through 4-21 for the phosphorus series and 4-22 through 4-26 for the nitrogen series. The plots show monthly and cumulative removals by constituent for all test cells.

Phosphorus

The general P removal trends observed over the treatment period at the ENR test cells continued in Q5 (Exhibit 4-17). At the northern site iron, control and aluminum treatments removed 80%, 56% and 83% of influent P load, respectively. Month to month results were quite variable for the STCs, but in keeping with results from previous quarters there was a net export of P with average removal rates -35% in the control cell and -10% in the Al treatment cell. The monthly averaged removal rates for the aluminum and iron treatments exhibited little variation during Q5 at the north site.

Phosphorus Species

A summary of each P-species is as follows:

- **TPP (Exhibit 4-18)**—patterns of removals for TPP are similar to those of TP at both locations. The NTCs show regular pattern of net removals on monthly and cumulative basis. The average TPP removal rate for the quarter was approximately 55% for the control, 80% for the iron treatment, and 85% for the aluminum treatment. The STCs exhibited month to month variation between positive and negative removal rates for control and treatment, consistent with results from the previous quarter.
- **TDP (Exhibit 4-19)**—All NTCs showed net TDP removal for the quarter, with the rates for treatment cells much higher than the control cell percent removal. Net

removal rates for the iron and aluminum treatment cells averaged 72% and 82%, respectively, versus 65% for the control (Exhibit 4-15). The STC control and treatment cell removal rates varied between positive and negative as in the previous the quarter. On a cumulative basis, however, the aluminum treatment (STC7) had a net positive removal rate, while the control (STC6) had a net negative rate.

- **SRP (Exhibit 4-21)**—The northern test cells sowed net removal for SRP over the quarter with removal rates of 77% for control and 90% for the two treatments. For the STCs SRP removal rates were variable month to month for both the treatment and control, but the net cumulative removal rate remained positive for both.

- **DOP (Exhibit 4-20)**—The month to month DOP removal rates are variable at NTC3, the control, but are moderate to high (40-90%) for the iron and aluminum treatments. These results are consistent with those observed for the previous quarter. For the STCs removal rates were variable on a monthly basis, but negative on a cumulative basis for the control and slightly positive for aluminum.

Nitrogen

A treatment effect is apparent at the NTCs for the fifth quarter and the previous quarters (Exhibits 4-16 and 4-22). TN removal averaged 37% for the iron treatment, 60% for the aluminum treatment, and 10% for the control cell. At the south site, the quarterly mean percent mass removal rate was 13% for aluminum but negative for the control.

Nitrogen Species

A summary of each N-species (TKN, TNOx, NH4-N, and Org-N) is as follows:

- **TKN (Exhibit 4-23)**— pattern and magnitude of removals for TKN closely duplicate those for TN at both sites.

- **TNOx (Exhibit 4-24)**—inflow and outflow [TNOx] are typically very low at the north site, therefore slight differences in the inflow versus outflow concentration result in fluctuation between positive and negative removals. At the south site both treatment and control had negative removal rates for the quarter.

- **NH4-N (Exhibit 4-26)**—for Q5 there was a high (80% – 89%) net removal of ammonia-N in all NTCs. Removal of NH4-N in the STC control (17%) and treatment cell (41%) were significantly less in comparison to the to previous quarters' performance.

- **TON (Exhibit 4-27)**—the quarterly TON removals were positive for NTCs. The quarter averaged rates were 15% for control , 33% for iron and 57% for aluminum and 16 % removal (north and south respectively). At the south the treatment cell averaged 29% removal, while the control's average rate was negative.

5.0 Phase 2 Operations at the Seminole Indian Reservation

The Cypress demonstration project is located on the Seminole Indian Reservation. The Phase II effort was separated into two parts. Part 1 included construction of hydraulic system components and a period of hydration and conditioning of the 4-acre wetlands demonstration area. The work completed included construction of the raw water pump and associated electrical work, transmission piping to the wetlands demonstration area, and a splash pad at the discharge point. Part 2 was to include construction of a chemical treatment system and a treatment pond and subsequent operation of the combined wetland and chemical treatment system. Wetland hydration began in late July 2000 and was scheduled to continue through December 2000.The Phase 2 project was halted in October 2000, however, at the request of the Seminole Tribe.

6.0 Marsh Readiness and Ionic Conditioning

One of the defining aspects of MWTS is the role of the wetland system in ameliorating the changes to the chemical signature of the water effected by chemical treatment. The concern is whether chemically treated waters are "marsh ready," that is, of acceptable quality to be discharged to the marshes of the Everglades ecosystem.

To date, the measures by which marsh readiness will be assessed have not been defined. There are several existing graphical methods for characterizing the chemistry of waters. Several of these approaches focus on ionic constituents, specifically anions and cations. The approaches include comparisons by stacked bar charts for anions and cations, pattern diagrams (e.g., Stiff diagrams) developed for oilfield drilling, log diagrams (Schoeller plots), radial charts, and trilinear plots.

For an initial comparison, modified Stiff diagrams were selected. The ionic parameters used in the Stiff diagrams are chloride, sulfate, bicarbonate, calcium, magnesium, and iron. The diagrams were developed by converting each ionic constituent concentration to a millequivalent value. Positively charged constituents were plotted on the left side of the diagram opposite negatively charged constituents on the right. Waters with comparable water quality will form similar shapes from connecting the resulting points (Todd, 1959). Masses, absolute values of the ion charge assumed for the constituents, and conversion factors are shown in Exhibit 6-1.

Exhibit 6-1.
Calculation data for conversion of concentration data (mg/l) to milliequivalents per liter (meq/l).

Constituent	Atomic Weight	Ion Charge	Conversion factor (divisor)
Chloride (Cl^-)	35.453	1	35.453
Sulfate (SO_4^{-2})	96.056	2	48.028
Bicarbonate (HCO_3^-)	61.016	1	61.016
Magnesium (Mg^{+2})	24.305	2	12.153
Calcium (Ca^{+2})	40.080	2	20.040
Iron (Fe^{+3})	55.847	3	18.616

Schoeller plots were also chosen to characterize the water chemistry in the MWTS. Ion concentrations, in milliequivalents per liter, are plotted on a logarithmic scale. The points generated are then joined by straight lines. If the line connecting two points in one sample is parallel to the same line from a different sample, then the ratio of ions in both water samples is equal (Todd, 1959).

Another method chosen to represent the water chemistry data is radial plotting. Ion concentrations, expressed in milliequivalents per liter, are plotted in counter-clockwise order. Radial plots are somewhat similar to Stiff diagrams in that the radially plotted points are connected to create a shape that can be used for comparing ionic concentrations of different water samples.

All three of these graphical methods are used to display and compare water quality results. Both the Stiff and the Radial plots create shapes that can be used to compare water quality between different samples. However, it is easier to detect when a water quality parameter deviates from other samples using the Schoeller plots. This is because Schoeller plots show both the absolute value of each chemical parameter and the concentration differences between samples (Todd, 1959).

Using each of the three methods described above, the chemical composition of all the MWTS NTC and STC were plotted for the calibration period of August 1999 through January 2000 (Exhibit 6-2, Exhibit 6-3, and Exhibit 6-4). Also using the methods described above, chemical composition for the MWTS NTCs and STCs for the period of March 2000 through September 2000, Quarter 4, and Quarter 5(treatment) were plotted (Exhibit 6-5 to 6-13). For comparison, the Loxahatchee National Wildlife refuge (WCA 1) (1996-1998), Water Conservation Area 2A (WCA-2A) (1996-1998), and Conservation area 3A (WCA-3A) (1977-1983)(SFWMD 2000, Swift and Nichols 1987) were plotted using the same methods (Exhibit 6-14, Exhibit 6-15, and Exhibit 6-16). It should be noted that all of the ions in all of the diagrams are expressed in milliequivalents per liter, except for iron, which is expressed as microequivalents per liter.

Diagrams of average values of ionic constituents for the six test cells for the pretreatment period August 1999 through January 2000 (Exhibits 6-2, 6-3, and 6-4) are very similar. The north site cells (NTCs) appear to have a slightly higher iron component values but the overall patterns are quite similar. Comparison of the calibration period diagrams with treatment period diagrams shows that treatment had little effect on ionic balances and ratios. Stiff, Schoeller, and radial plots are provided for the test cells for Q4 (Exhibit 6-8, 6-9, and 6-10) and Quarter 5 (Exhibit 6-11, 6-12, and 6-13). A cell by cell comparison for the last two quarters shows similar patterns to the ionic signature in both quarters. During Quarter 4, the iron treatment cell (NTC –2) had increased iron and chloride concentration, skewing the diagram for that cell somewhat. Iron at NTC-2 decreased during Quarter 5, but the chloride content increased. Otherwise, the ionic signature of the two treatment cells was very similar to that of the control cell.

A comparison of the test cell data with data from the Water Conservation Areas is a useful method of extending the comparison to consider the question of overall "marsh readiness" of the water. The three plots comparing the WCAs show that constituent concentrations differ between the respective conservation areas. The Schoeller plots (Exhibit 6-15), however, indicate that ratios of ions are similar for WCA 1 and WCA 2. Comparison of the MWTS test cells treatment period data with WCA data suggests that the ionic condition of test cell's effluent is very similar to that found in the interior of WCA 2. The exception is NTC-2, the iron treatment.
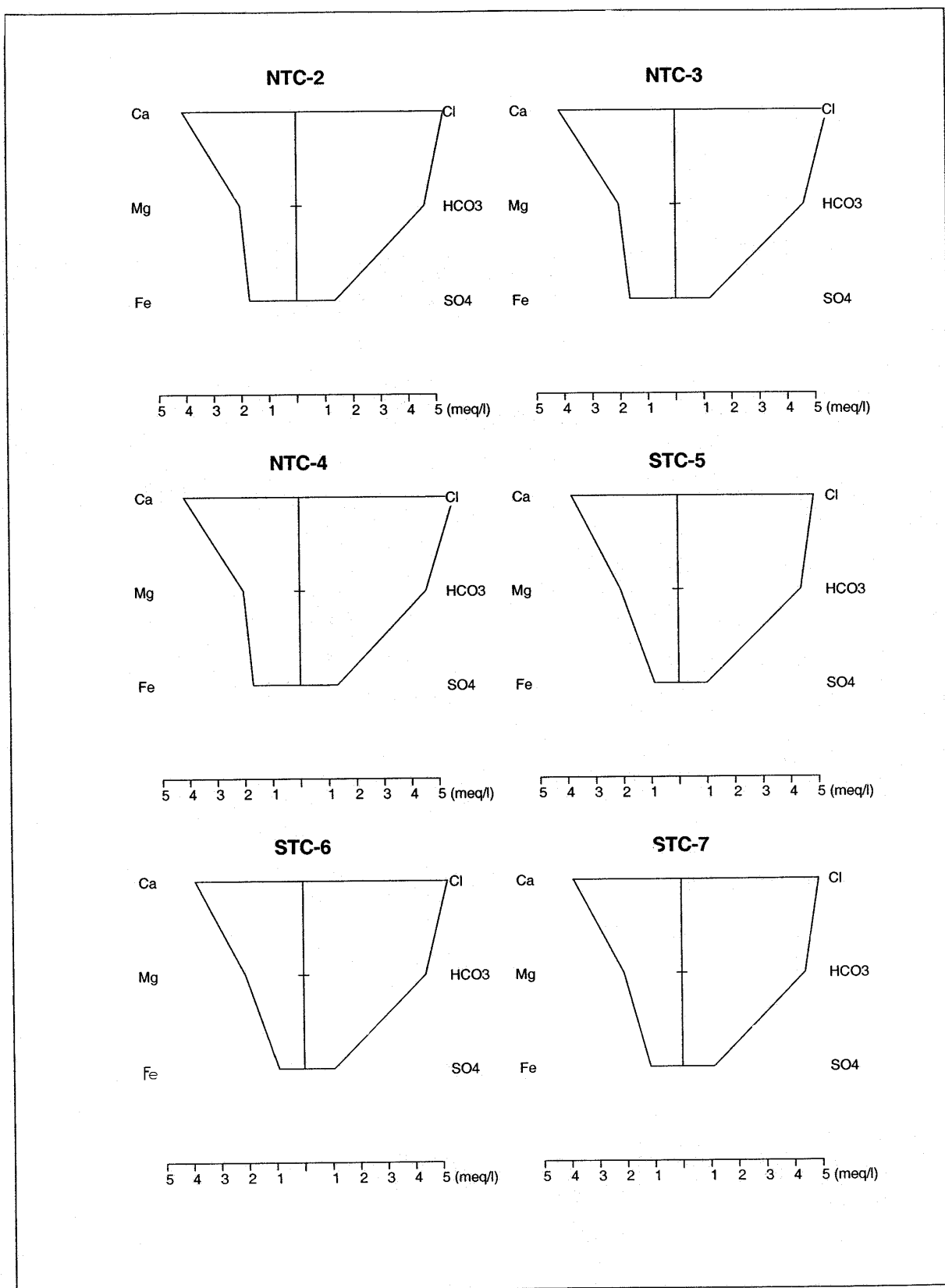
NTC-2

NTC-3

NTC-4

STC-5

STC-6

STC-7

Exhibit 6-2 Stiff Diagrams Showing the Chemical Composition of the MWTS Test Cells from August 1999 - January 2000 (calibration period)

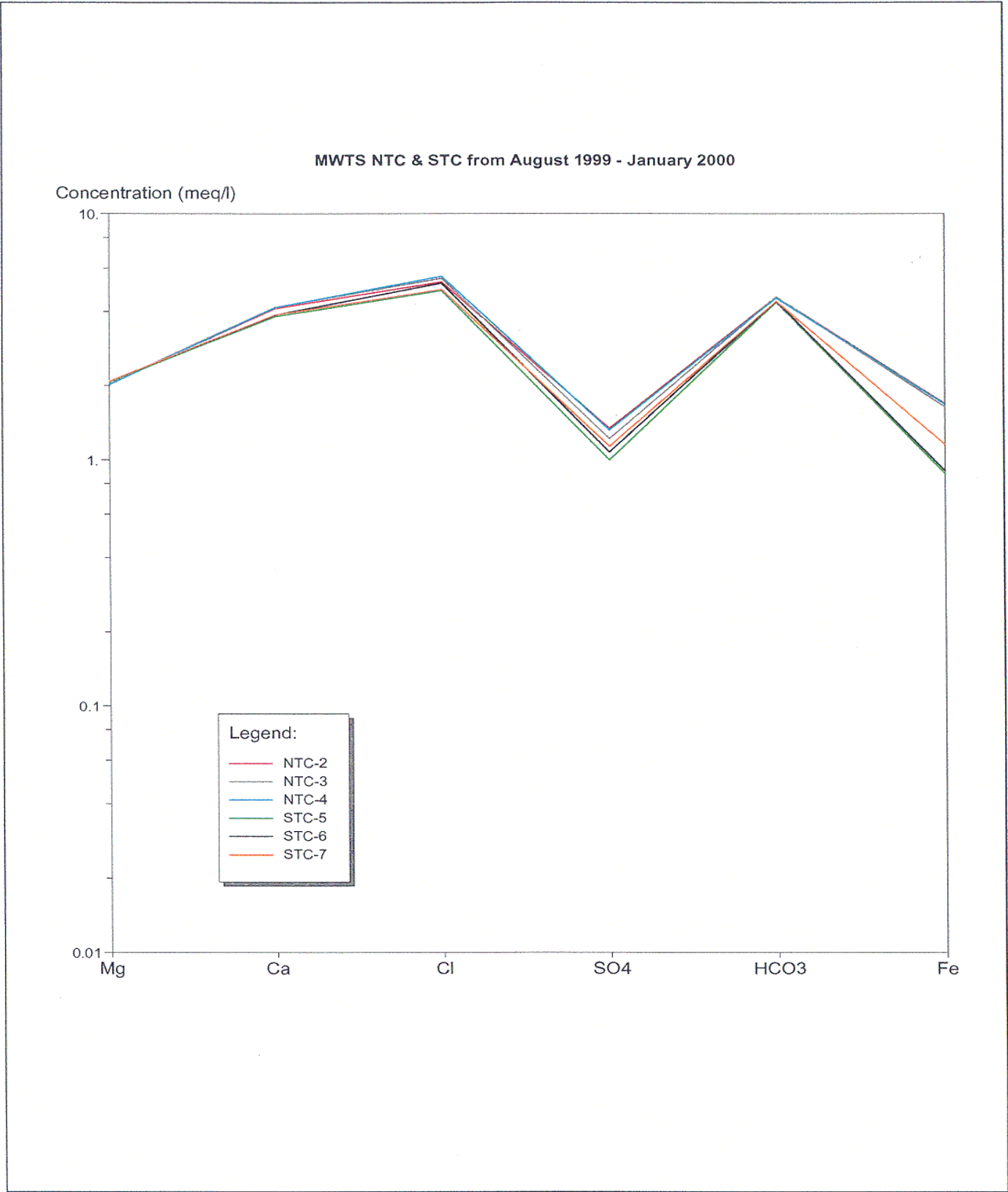**MWTS NTC & STC from August 1999 - January 2000**

Concentration (meq/l)

Legend:
- NTC-2
- NTC-3
- NTC-4
- STC-5
- STC-6
- STC-7

Mg Ca Cl SO4 HCO3 Fe

Exhibit 6-3 Schoeller Plots Showing the Chemical Composition of the MWTS from August 1999 - January 2000 (calibration period)
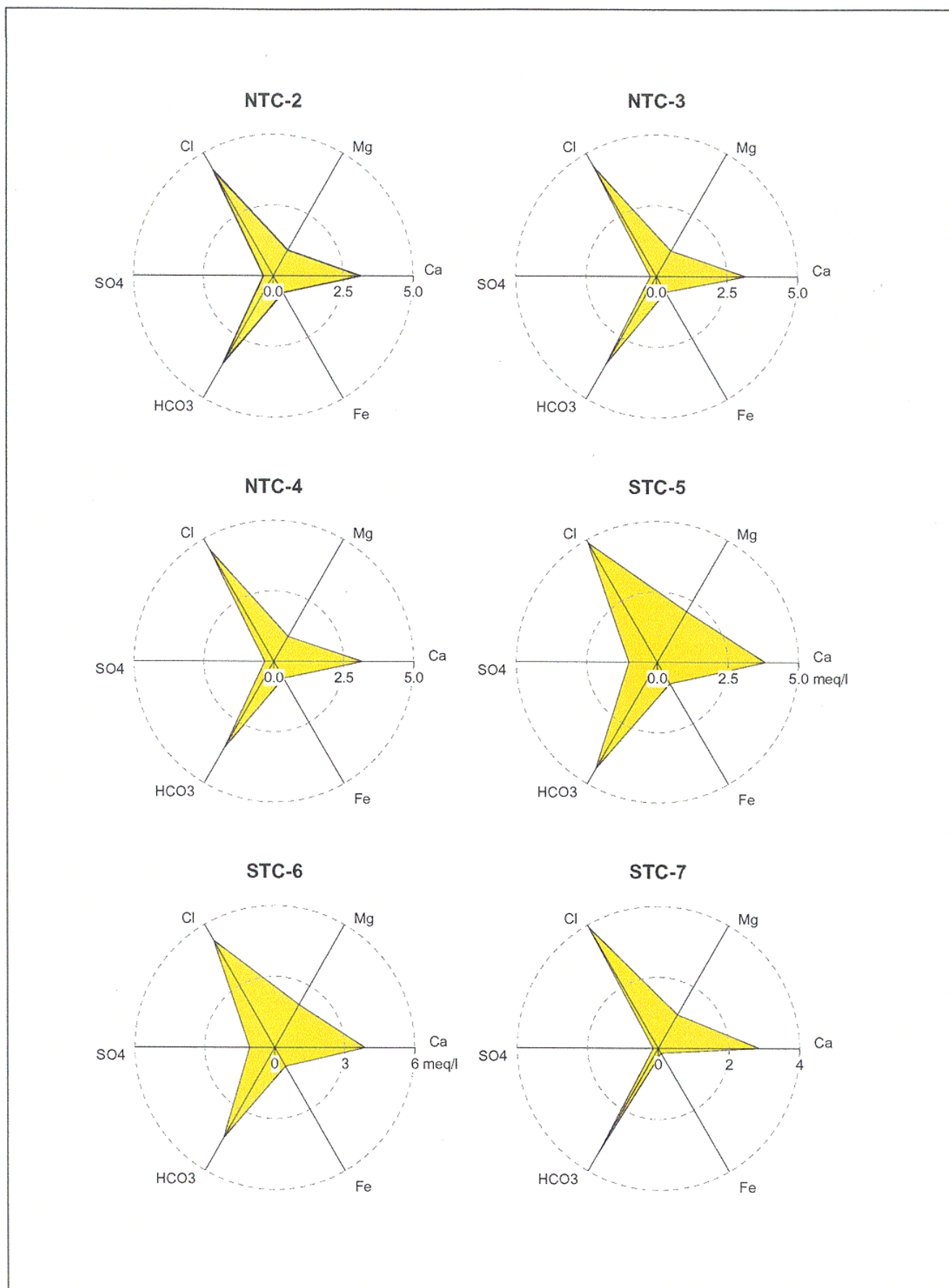
Exhibit 6-4 Radial Plots Showing the Chemical Composition of the MWTS from August 1999 - January 2000 (calibration period)
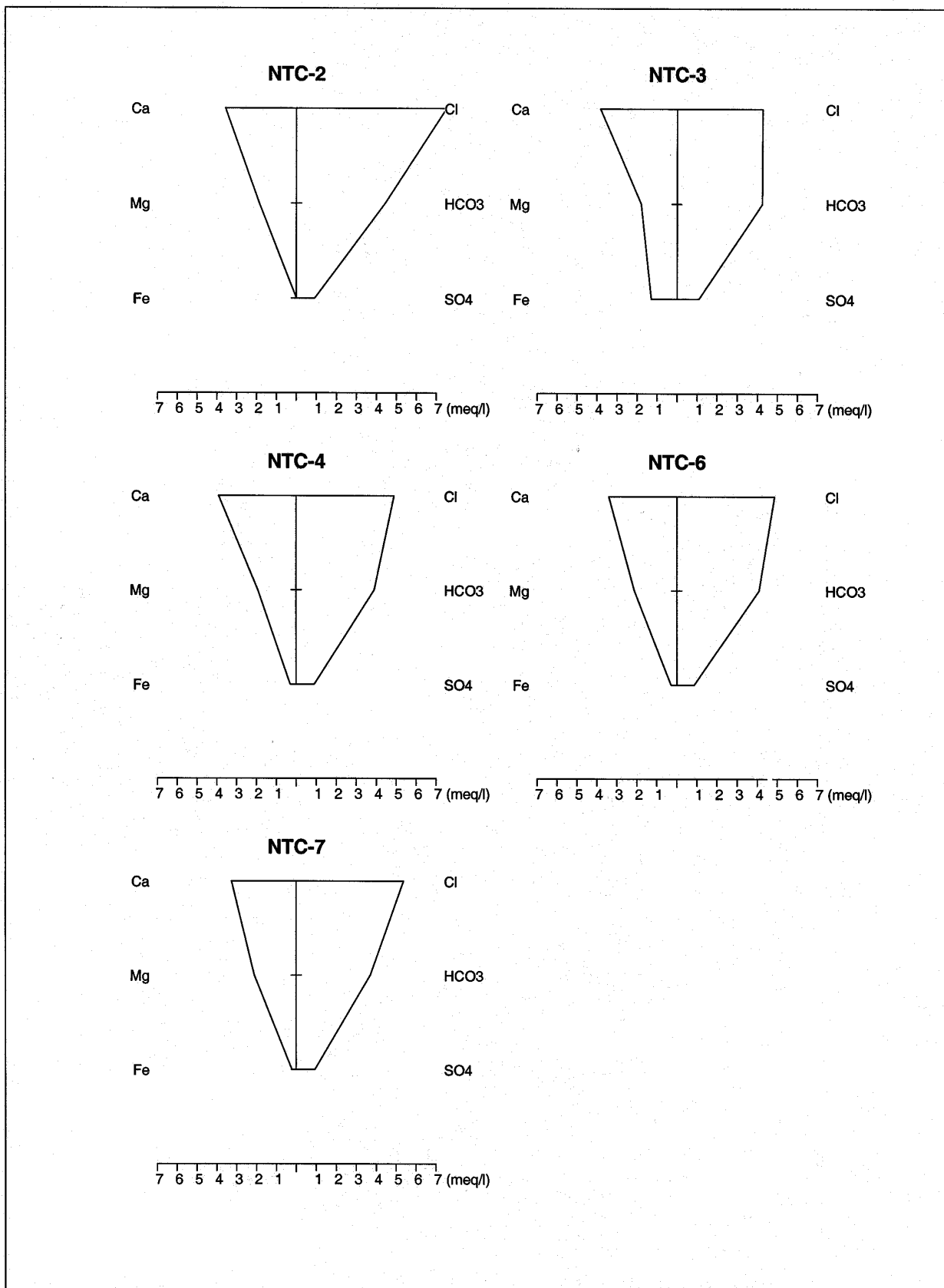
Exhibit 6-5 Stiff Diagrams Showing the Chemical Composition of the MWTS from March 2000 - September 2000 (treatment period)

MWTS NTC & STC from March 2000 - September 2000

Concentration (meq/l)

Legend:
- NTC-2
- NTC-3
- NTC-4
- NTC-6
- NTC-7

Mg Ca Cl SO4 HCO3 Fe
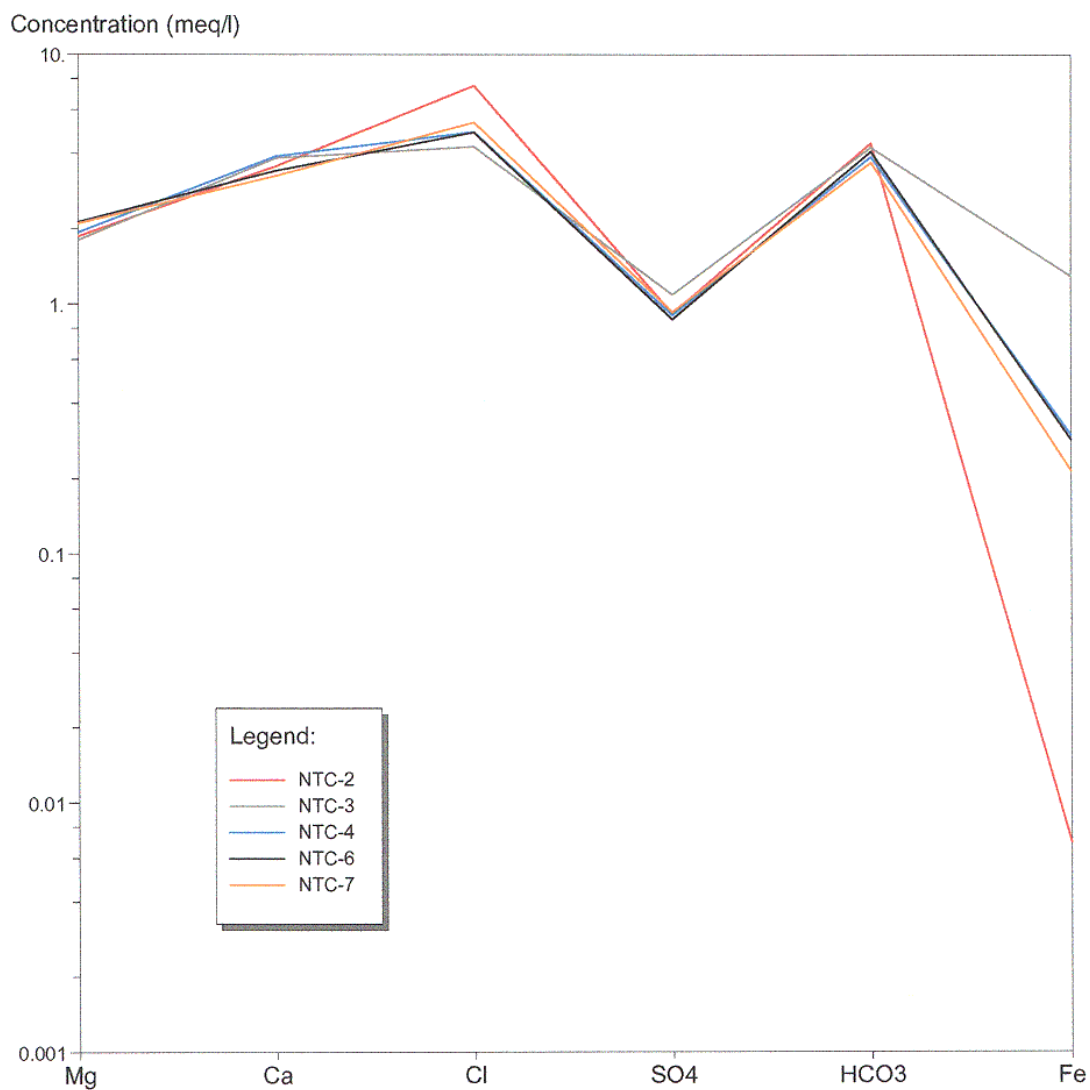
Exhibit 6-6 Schoeller Diagrams Showing the Chemical Composition of the MWTS from March 2000 - September 2000
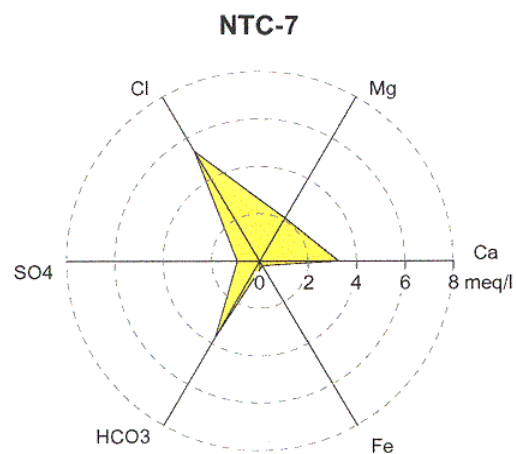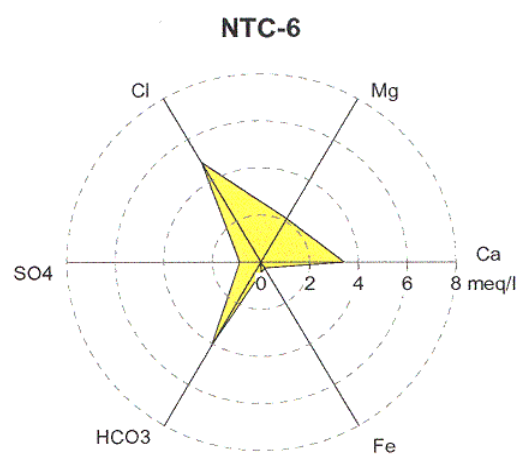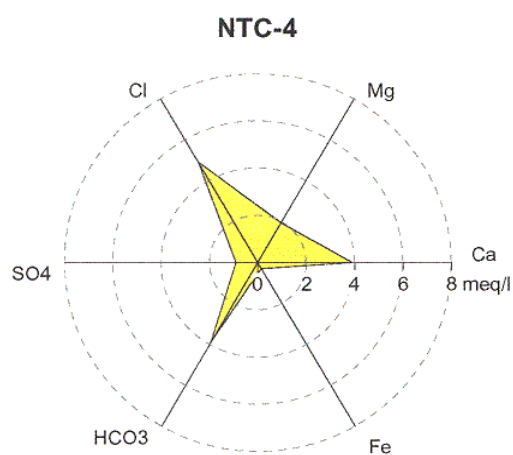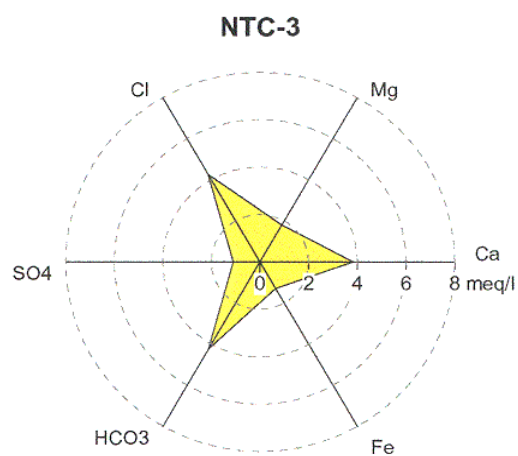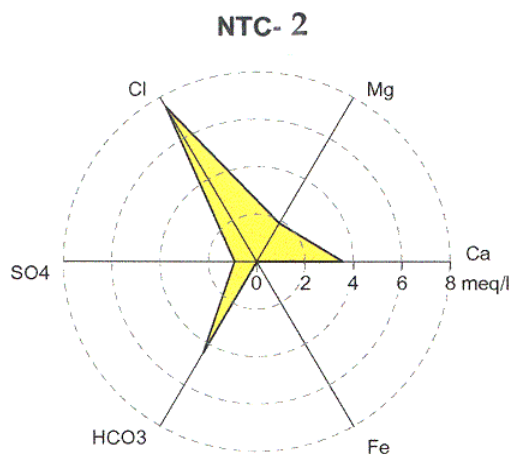
Exhibit 6-7 Radial Diagrams Showing the Chemical Composition of the MWTS from March 2000 - September 2000 (treatment period)
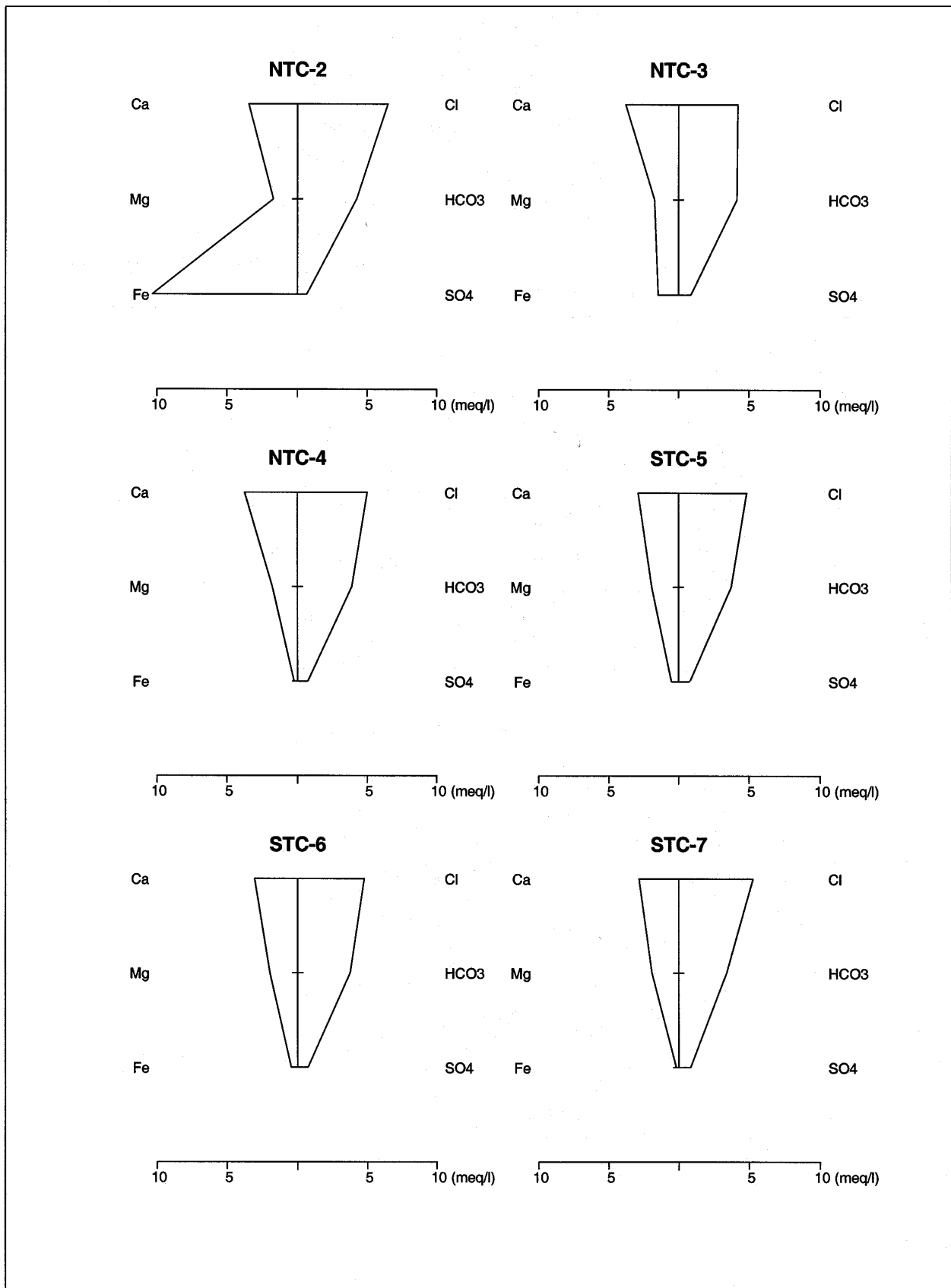
Exhibit 6-8 Stiff Diagrams Showing the Chemical Composition for the MWTS Test Cells for Q4
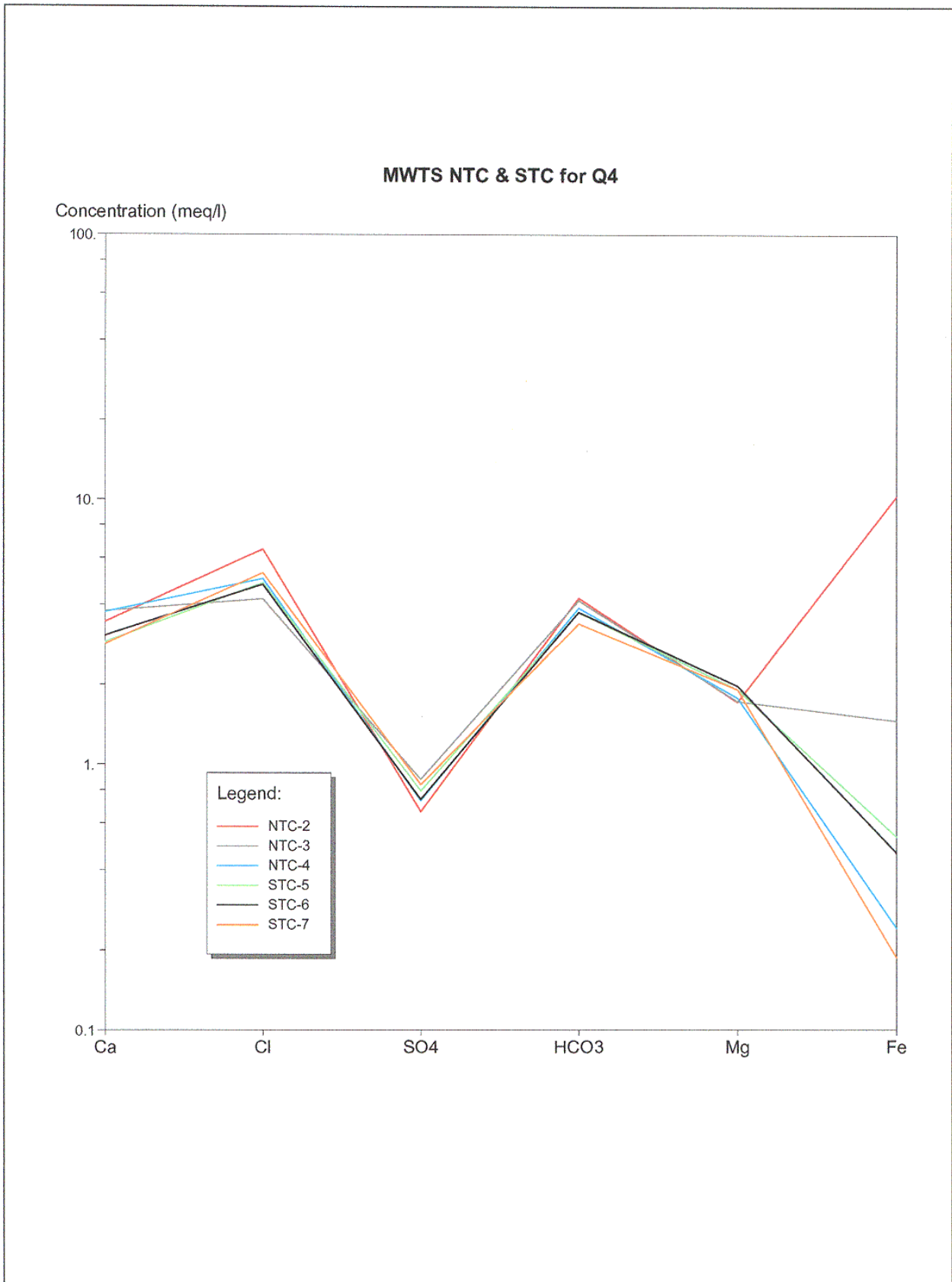
Exhibit 6-9 Schoeller Diagram Showing the Chemical Composition of the MWTS Test Cells for Q4
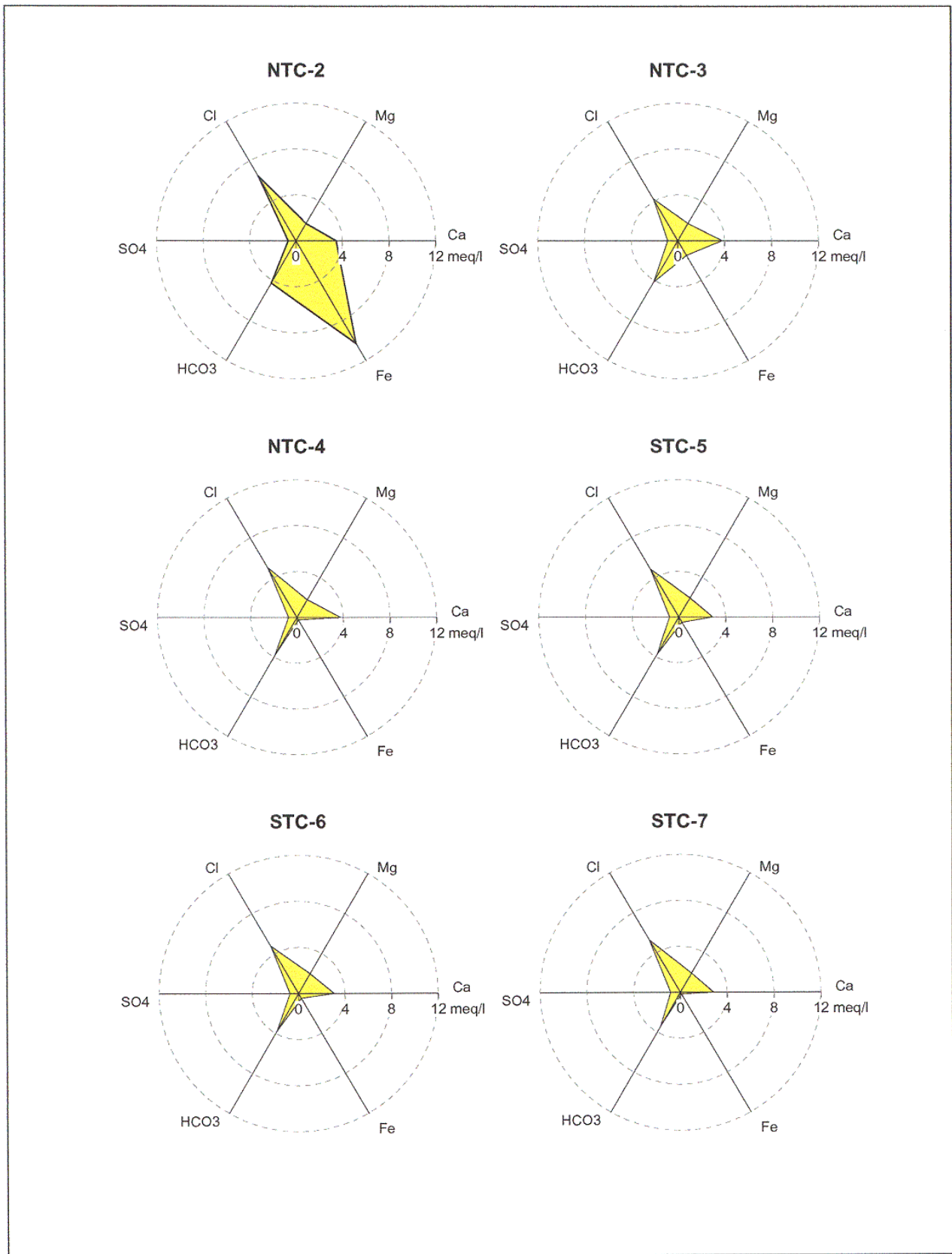
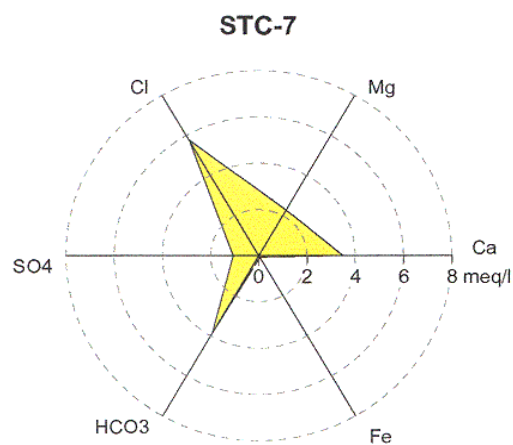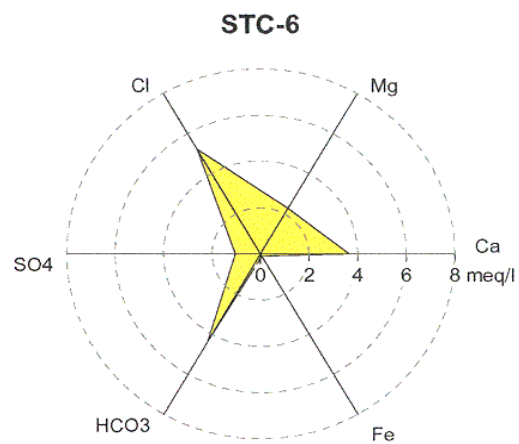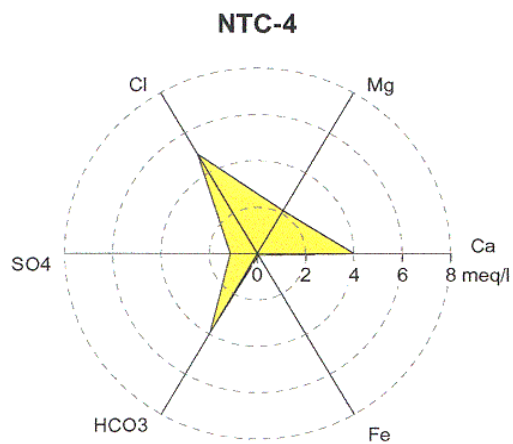Exhibit 6-10 Radial Plots Showing Chemical Composition of MWTS Test Cells for Q4
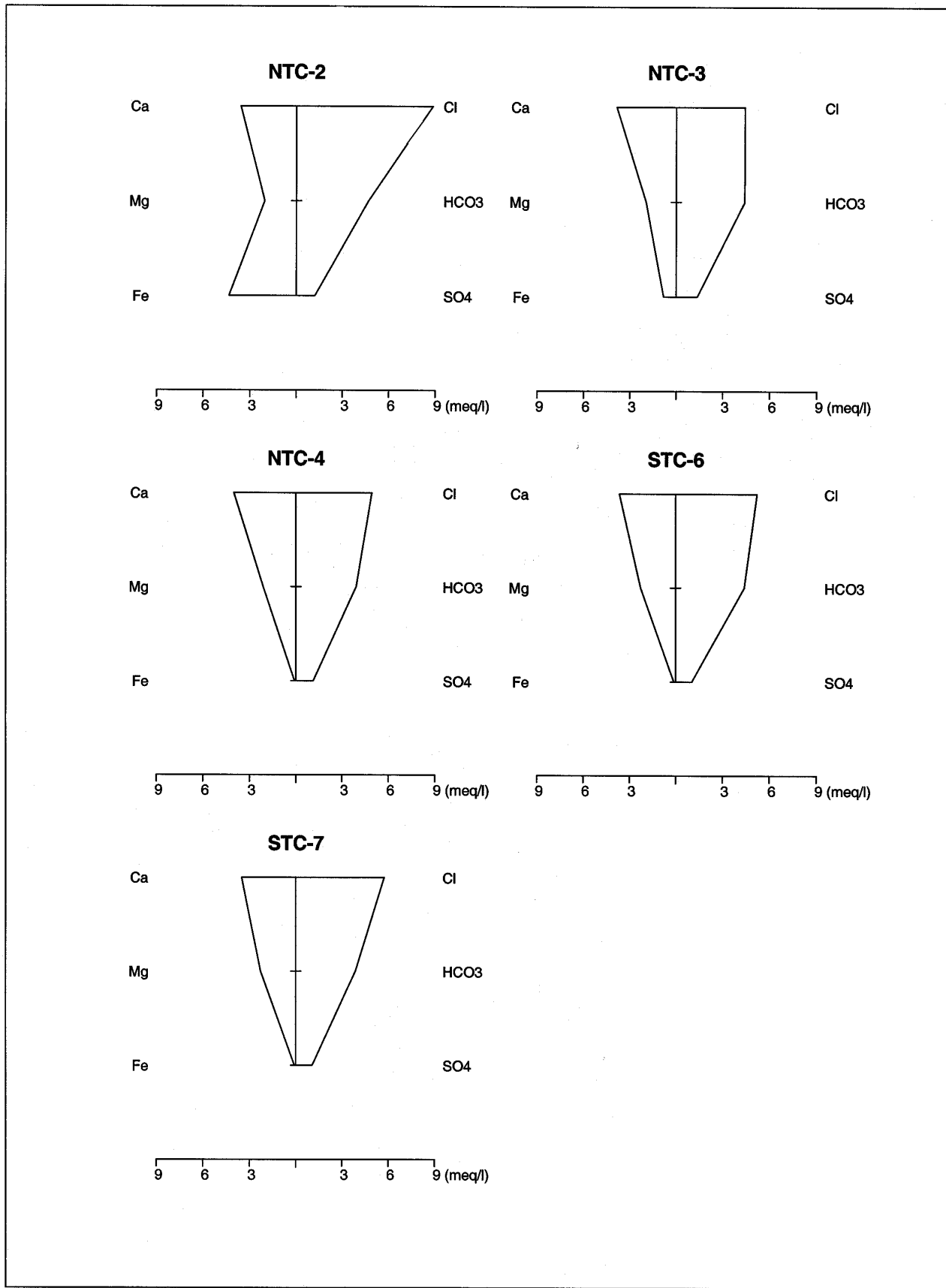
Exhibit 6-11 Radial Plots Showing Chemical Composition of MWTS Test Cells for Q5

MWTS NTC & STC for Q5

Concentration (meq/l)

Legend:
— NTC-2
— NTC-3
— NTC-4
— STC-5
— STC-6
— STC-7

Ca   Cl   SO4   HCO3   Mg   Fe
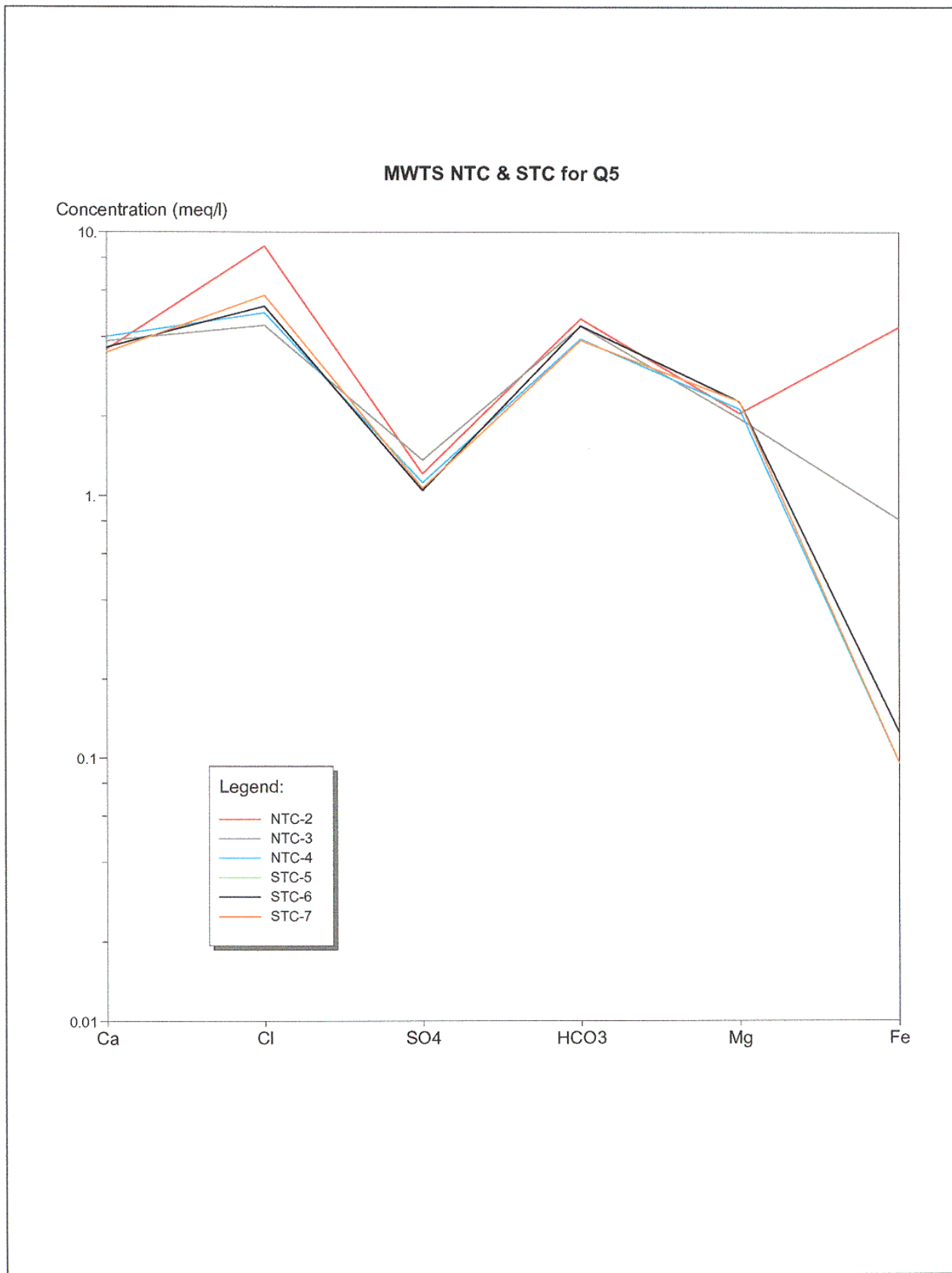
Exhibit 6-12 Schoeller Plot Showing the Chemical Composition of MWTS Test Cells for Q5
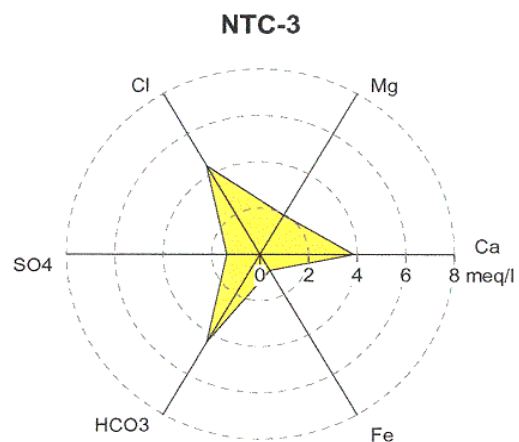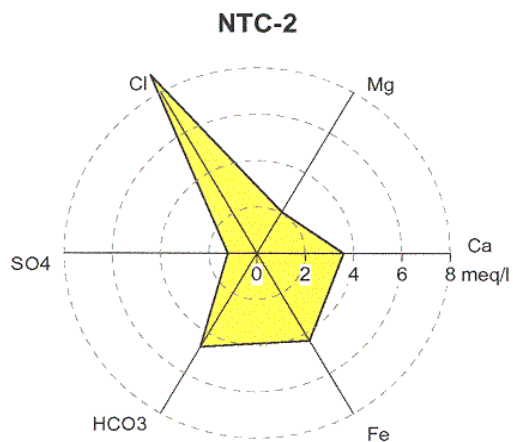
Exhibit 6-13 Radial Plots Showing the Chemical Composition of MWTS Test Cells for Q5

WCA-1
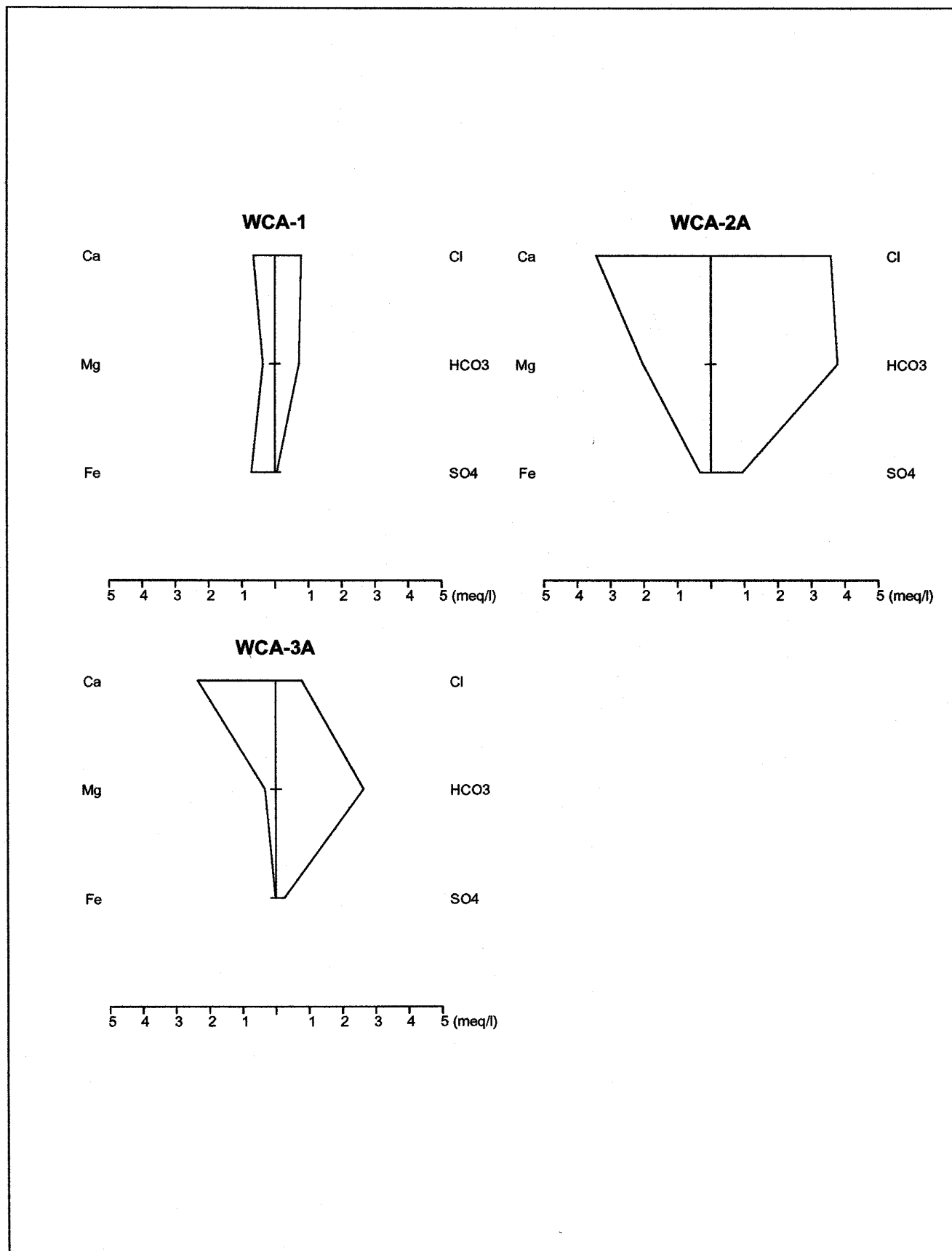
Ca		Cl
Mg		HCO3
Fe		SO4

5 4 3 2 1   1 2 3 4 5 (meq/l)

WCA-2A

Ca		Cl
Mg		HCO3
Fe		SO4

5 4 3 2 1   1 2 3 4 5 (meq/l)

WCA-3A

Ca		Cl
Mg		HCO3
Fe		SO4

5 4 3 2 1   1 2 3 4 5 (meq/l)

Exhibit 6-14 Stiff Diagrams Showing the Chemical Composition of the Water Conservation Areas
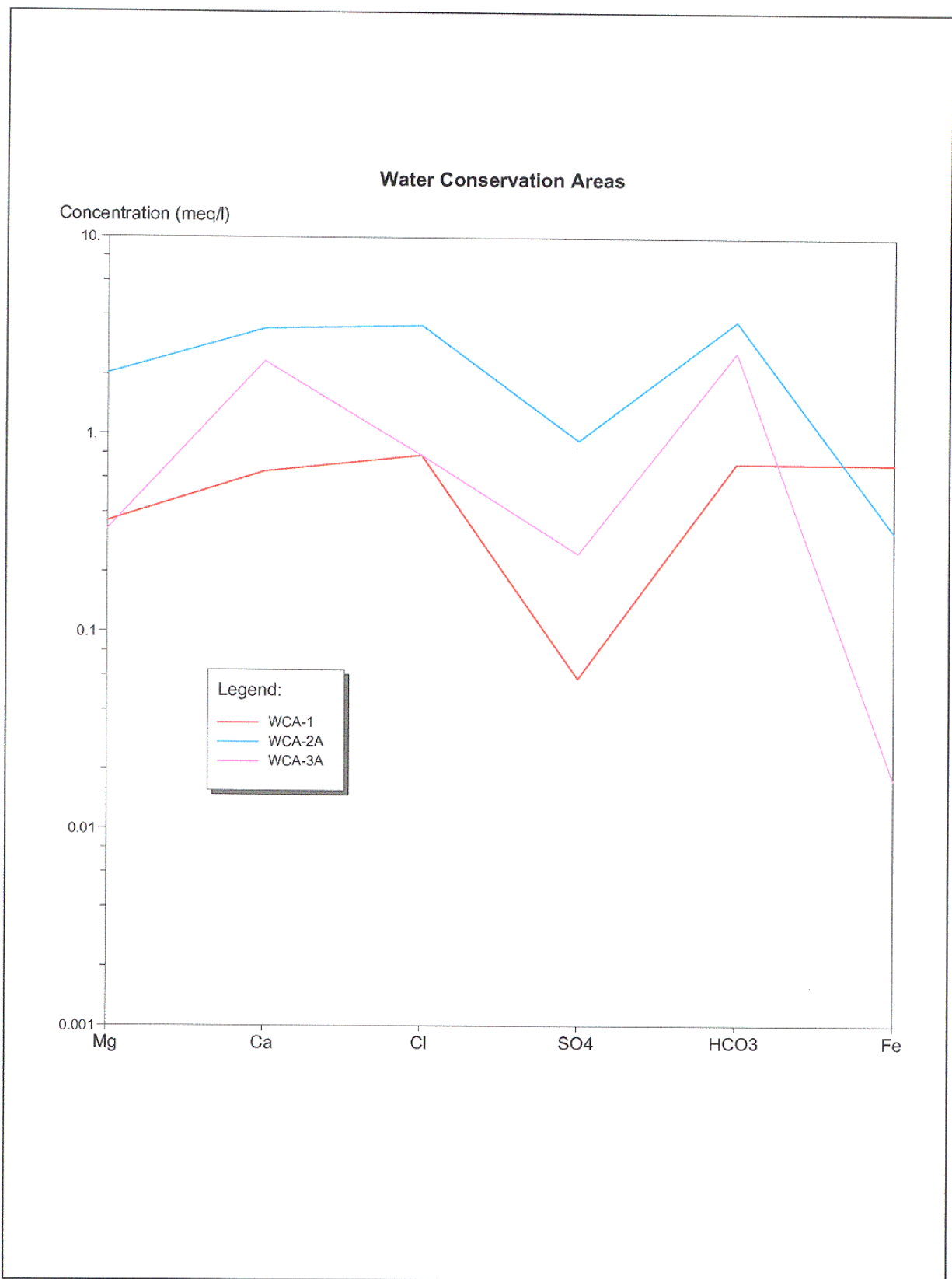
Exhibit 6-15 Schoeller Diagram Showing the Chemical Composition of the Water Conservation Areas
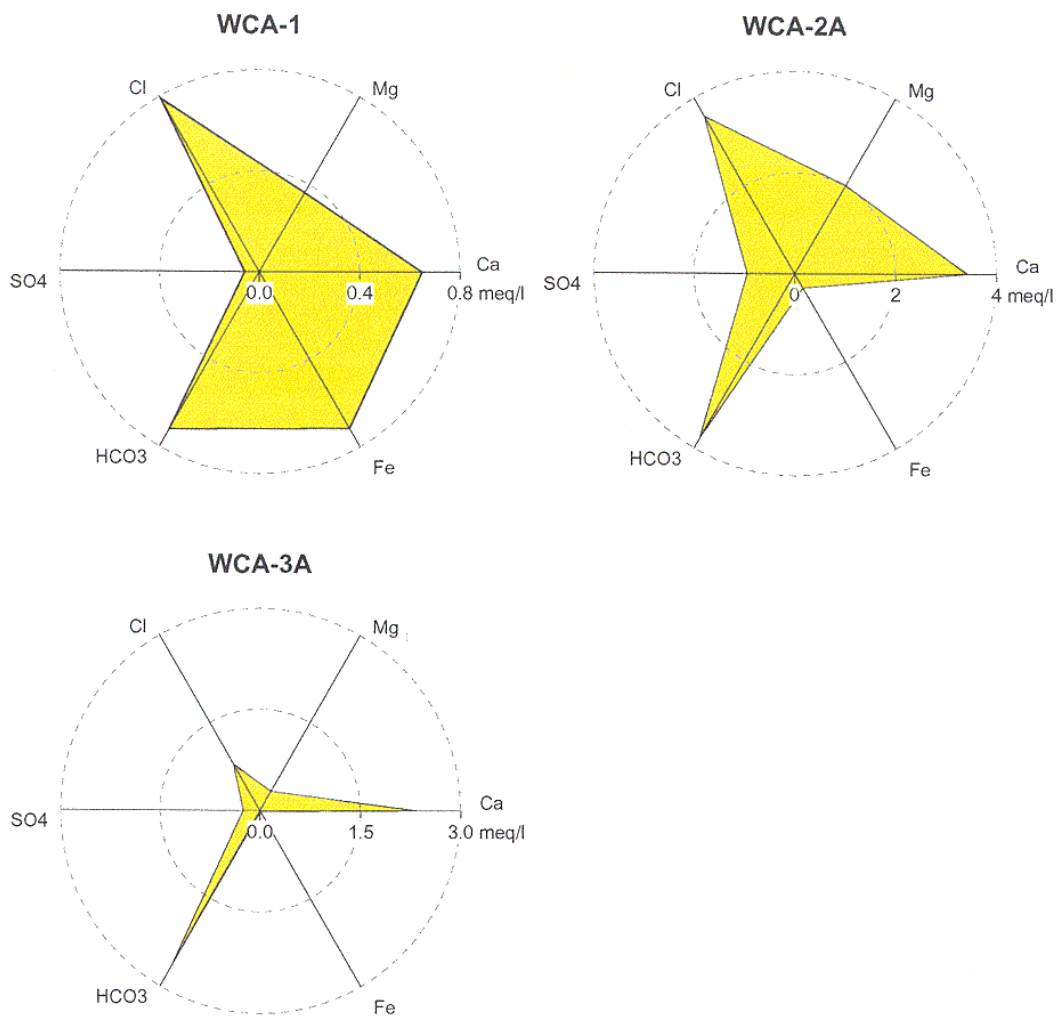
Exhibit 6-16 Radial Plots Showing the Chemical Composition of Water Conservation Areas

7.0 References

McCormick, Paul V., Susan Newman, Garry Payne, ShiLi Miao, and Thomas Fontaine. 2000. Chapter 3: Ecological Effects of Phosphorus Enrichment in the Everglades. Everglades Consolidated Report. Garth Redfield (Editor) South Florida Water Management District, 3301 gun Club Road, West Palm Beach, FL 33416-4680.

Swift, David R. and Robert B. Nicholas. 1987. Periphyton and Water Quality Relationships in the Everglades Water Conservation Areas 1978 – 1982. Technical Publication 87-2. Environmental Sciences Division, Resource Planning Department, South Florida Water Management District, West Palm Beach, FL. 44 pp.

Todd, David K. 1959. Groundwater Hydrology. John Wiley & Sons, Inc. New York, NY. 535 pp.

Water Regime Time Series Charts

Note:

- ➢ North Test Cells
  - Test Cell 2 =   NTC 2   iron (Fe) treatment cell
  - Test Cell 3 =   NTC 3   control cell
  - Test Cell 4 =   NTC 4   aluminum (Al) treatment
- ➢ South Test Cells
  - Test Cell 5 =   STC 5   control cell
  - Test Cell 6 =   STC 6   control cell
  - Test Cell 7 =   STC 7   aluminum (Fe) treatment cell

Water Quality Time Series Charts

Note:

- ➢ North Test Cells
    - ▪ NTC 2   iron (Fe) treatment cell
    - ▪ NTC 3   control cell
    - ▪ NTC 4   aluminum (Al) treatment
- ➢ South Test Cells
    - ▪ STC 5   control cell
    - ▪ STC 6   control cell
    - ▪ STC 7   aluminum (Fe) treatment cell

Quarterly Boxplot Charts

Note:

- ➢ North Test Cells
  - Cell 2 = NTC 2   iron (Fe) treatment cell
  - Cell 3 = NTC 3   control cell
  - Cell 4 = NTC 4   aluminum (Al) treatment
- ➢ South Test Cells
  - Cell 5 = STC 5   control cell
  - Cell 6 = STC 6   control cell
  - Cell 7 = STC 7   aluminum (Fe) treatment cell

APPENDIX C
Water Quality Gradient Time Series Charts

Note:

- ➢ North Test Cells
    - ▪ NTC 2   iron (Fe) treatment cell
    - ▪ NTC 3   control cell
    - ▪ NTC 4   aluminum (Al) treatment
- ➢ South Test Cells
    - ▪ STC 5   control cell
    - ▪ STC 6   control cell
    - ▪ STC 7   aluminum (Fe) treatment cell

Memorandum – North Test Pilot Unit Evaluation